

Discontinuous precipitation of Cr₂N in a high nitrogen, chromium–manganese austenitic stainless steel

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The main purpose of the present work is to study the effect of a high nitrogen content (1 wt% N), on the microstructural evolution of a Cr–Mn austenitic stainless steel aged over the [400–900 °C] temperature interval. Thermal treatments carried out between 700 and 900 °C lead to the decomposition of the nitrogen supersaturated austenitic matrix by discontinuous precipitation of Cr₂N particles. The microstructural features of the reaction are described and analysed. In the present case, the cellular precipitation of Cr₂N is a peculiar and complex phenomenon which involves two diffusion mechanisms: the diffusion of an interstitial element (nitrogen) and the diffusion of a substitutional one (chromium). The nucleation of the discontinuous precipitation arises from a reduction of the surface energy of the precipitates. Furthermore, the precipitation growth is a non-steady state process, because the reaction is governed at first by the intergranular diffusion of chromium, and then tends to be controlled by its bulk diffusion. Consequently, the features of this discontinuous precipitation do not fit in with the assumptions of usual theories, which have been established for binary substitutional systems that transform in steady state conditions. This discontinuous precipitation brings about a slight hardening. Then, the hardness of the aged samples can be described by an additive relationship between the hardness of the precipitation cells and that of the untransformed matrix. Beside the discontinuous precipitation of Cr₂N, sigma phase forms with significant volume fractions.

1. Introduction

High nitrogen austenitic stainless steels are very promising for numerous engineering properties [1, 2]. Alloying with nitrogen beyond the solubility limit markedly increases the yield strength of austenitic stainless steels, without any substantial loss of toughness [1, 3–6]. This outstanding effect opens up new fields of applications for these steels, at low [2] as well as at high [7] temperatures. However, the mechanisms of action of nitrogen upon the microstructure and its stability, and therefore, upon the chemical, physical and mechanical properties are not clearly understood. With a view to their potential applications at temperatures higher than 600 °C (retaining rings, turbine blades etc.), it seems particularly pertinent to investigate the influence of a very high content of nitrogen (1 wt%) on the microstructural evolution of not prestrained austenitic stainless steels during thermal treatments. Studies of the precipitation reactions in not prestrained, high nitrogen austenitic steels are very scarce. Most of the works limit themselves to an identification of the precipitates and to a characterization of the overall kinetics of the precipitation. The present reflections prove the utility of this study.

Generally speaking, the ageing treatments of austenitic stainless steels, carried out between 500 and 900 °C induce a precipitation of carbides, nitrides and carbonitrides, as well as intermetallic compounds such as sigma, chi or eta phases [8]. These concurrent precipitation phenomena are numerous and therefore not easily distinguishable from one another. Moreover they depend strongly on the chemical composition of the alloys, and/or on the thermomechanical treatments before ageing. In particular, high interstitial contents change the typical schemes of precipitation. A carbon or a nitrogen supersaturation gives rise to the decomposition of the matrix, by a grain boundary discontinuous precipitation of carbonitrides, with a quasi-pearlitic appearance. The chemical composition of the precipitates is governed by the nature of the most frequent interstitial element, carbon or nitrogen. For instance, if the carbon content overcomes the nitrogen one, the precipitates are of the M₂₃(CN)₆ type [9]. By way of contrast, the precipitates are of Cr₂N type in case of a prevailing nitrogen content [10, 11]. This kind of precipitation is often called “nitrogenous pearlite”. However, this denomination is inaccurate because of the non-eutectoidic mechanism of the reaction.

The aim of the present work is to emphasize the peculiarities of the discontinuous precipitation of Cr₂N, in a high nitrogen, chromium–manganese austenitic steel. This investigation deals successively with the nucleation and growth stages. Finally, the paper considers the effect of this precipitation on the hardness of the steel.

2. Experimental procedure

Table I gives the chemical composition of the alloy. The manufacturing processes of high nitrogen steels need peculiar precautions [12–15]. In order to obtain nitrogen levels beyond the solubility limit, both the steel making technology and the steel composition must be modified. The 0.9 wt % N austenitic steel was elaborated by Vereinigte Schmiedewerke GmbH, under high nitrogen pressure in a pressurized electrosag remelting facility. Moreover, high chromium (18 wt %) and high manganese (19 wt %) contents are required, because these two elements are known to lower the activity of nitrogen, and consequently, to increase the solubility limit of nitrogen in the melt [16].

Heat treatments were given under stagnant air to transverse slices cut from 25-mm diameter bars. All the samples were first homogenized at 1150 °C for 30 min, before being water cooled to room temperature. One hour thermal treatments were subsequently carried out between 400 and 900 °C. In addition, complementary 800 °C ageing treatments were performed for various times up to 150 h. The microstructural investigation was achieved with specimens sufficiently polished or sawn, so as to remove the nitrogen-depleted surface case. The thickness of this nitrogen impoverished layer was calculated from the diffusion coefficient of nitrogen in γ iron [17].

X-ray diffractometry (XRD), light, scanning (SEM) and transmission (TEM) electron microscopy were used for the microstructural studies. Before metallographic investigations, the samples were etched during about 1 or 2 min in a solution composed of 20% nitric acid, 40% hydrochloric acid and 40% glycerol by volume. K α radiation was used for diffractometry so as to quantify the relative volume fraction of austenite in matrix and in interlamellar spacings. The grain size was measured by optical micrography using the linear intercept method applied to more than 200 grains. This evaluation took no account of the existence of annealing twins. This procedure of measurement was also applied in order to estimate the interlamellar spacing in the cells of precipitation. In each ageing condition, more than 1000 measurements were performed in the only domains where the lamellae are strictly parallel. The volume fraction of the cells of discontinuous precipitation is assumed equal to its surface fraction, because of the great number (about

500) of grains investigated that averages the three-dimensional unevenness of the precipitation [18]. The surface fraction of cells was quantified by planimetry on light micrographs.

Thin foils for transmission electron microscopy were prepared by mechanical grinding down to 80 μ m, and finished by a twin-jet electrochemical polishing. This latter step was performed at about 15 °C and 3.5×10^{-2} A mm⁻² in a 90% acetic acid and 10% perchloric acid solution. The scanning transmission electron microscopy (STEM) and energy dispersive spectroscopy (EDX) analyses were conducted with small probe sizes close to 3 nm due to the high 300 kV accelerating voltage.

Mechanical properties were characterized by 30 kg and 25 g Vickers Hardness measurements.

3. Results

3.1. Microstructural features of the discontinuous precipitation of Cr₂N

Fig. 1 shows the microstructure of the alloy in the solution-treated condition. The steel displays a fully austenitic structure with an average grain size of about 80 μ m. Moreover, the sample exhibits numerous annealing twins. This crystallographical feature is typical of well-recrystallized f.c.c. metals with rather low stacking fault energy. Furthermore, it is worth emphasizing that the as-quenched samples do not contain any grain boundary precipitates. Only scarce spheroidal nitrides smaller than 100 nm remain inside the grain. Table II shows the main characteristics of the solution-treated alloy.

One hour ageing treatments performed at temperatures lower than 700 °C are ineffective on the microstructure. On the contrary, the thermal treatments carried out at higher temperatures (between 700 and 900 °C) lead to the formation of precipitation cells on

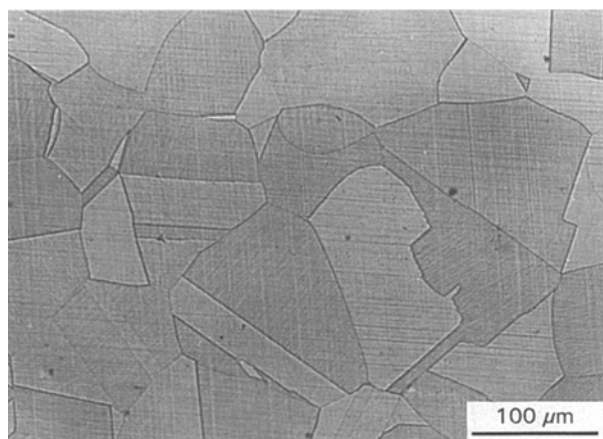


Figure 1 Water quenched (1150 °C, 30 min) microstructure.

TABLE I Chemical composition of the alloy (in wt %)

C	N	Cr	Mn	V	Si	Mo	Ni
0.06	0.9	18	19	0.12	0.4	0.06	0.05

TABLE II Properties of the as-quenched state

lattice parameter (nm)	0.3622 ± 0.0003
grain size (μ m)	82 ± 15
hardness (H _v , 30 kg)	254 ± 5
microhardness (H _v , 25 g)	434 ± 15

some austenitic grain boundaries (Fig. 2). This phenomenon is particularly obvious in the sample aged at 800 °C, which contains about 8% of domains of precipitation (Fig. 2(b)). According to this observation, the precipitation is much less marked in the specimens treated at 700 or 900 °C (Fig. 2(a) and (c)). As exemplified by the SEM micrograph in Fig. 3, the investigations achieved at higher magnifications prove the two-phase aspect of the cells.

In other respects, the reaction of precipitation is accompanied by a grain growth over the [700–900 °C] temperature interval (Fig. 4). This feature is not surprising because discontinuous precipitation reactions are known to arise from a combination between heterogeneous precipitation at grain boundaries and concurrent migration of those boundaries [19].

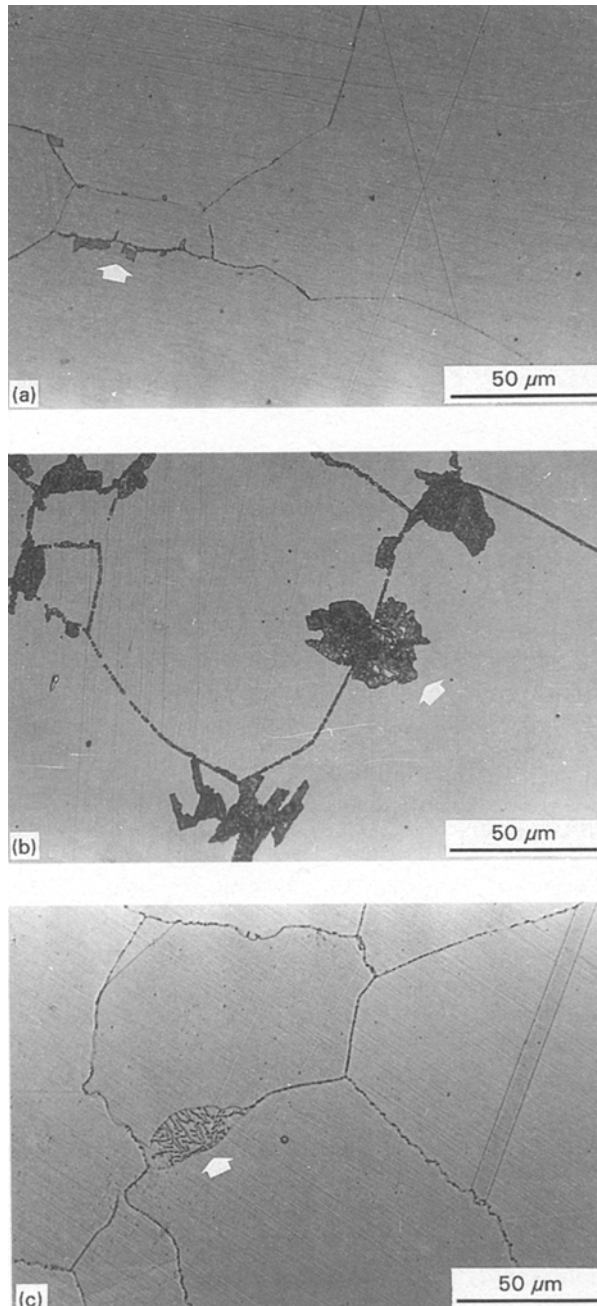


Figure 2 Effect of ageing temperature on discontinuous precipitation. (a) 700 °C for 1 h. (b) 800 °C for 1 h. (c) 900 °C for 1 h.

If the duration of ageing at 800 °C is increased from 1 to 150 h, the precipitation cells of Cr₂N tend to invade almost all the sample (Fig. 5). However, Fig. 6 strongly suggests that the discontinuous precipitation of Cr₂N is not complete. Indeed, it can be noted that the volume fraction of cells grows very quickly during the first 50 h of ageing at 800 °C and then stabilizes at a level close to 80%.

TEM and XRD allow a thorough characterization of the domains of precipitation. TEM shows that the cells comprise alternate lamellae of Cr₂N and of an

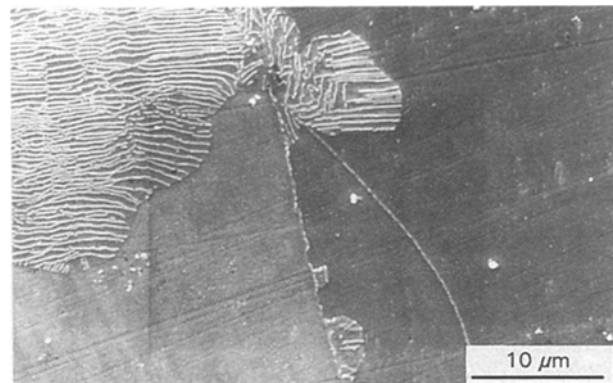


Figure 3 Biphase aspect of cells of discontinuous precipitation.

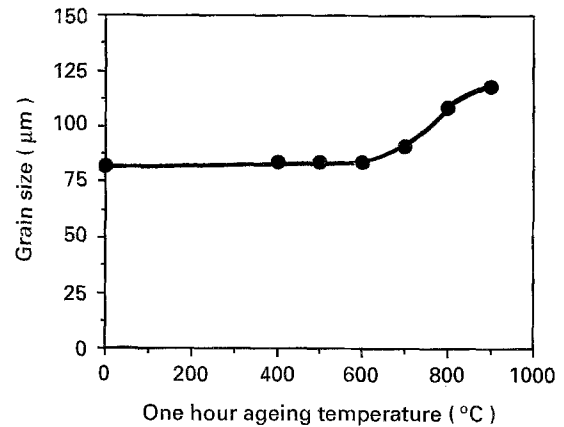


Figure 4 Effect of ageing temperature on the grain size of austenite.

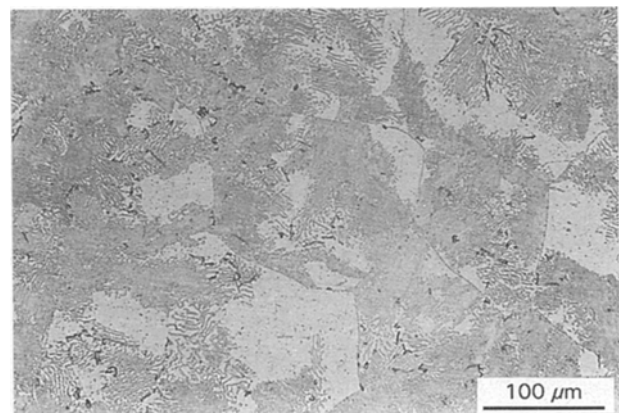


Figure 5 High but not full volume fraction of the cells of precipitation in the sample aged for 150 h at 800 °C.

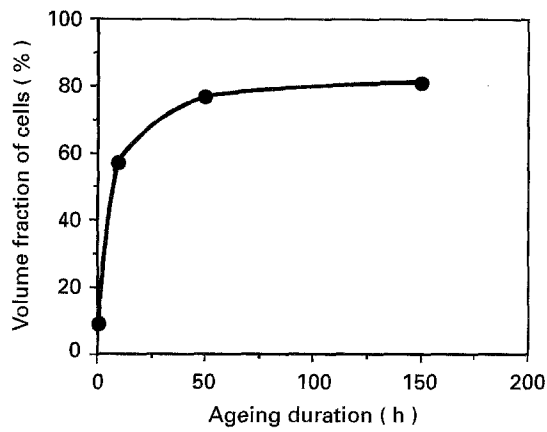


Figure 6 Kinetics of growth of the volume fraction of cells at 800 °C.

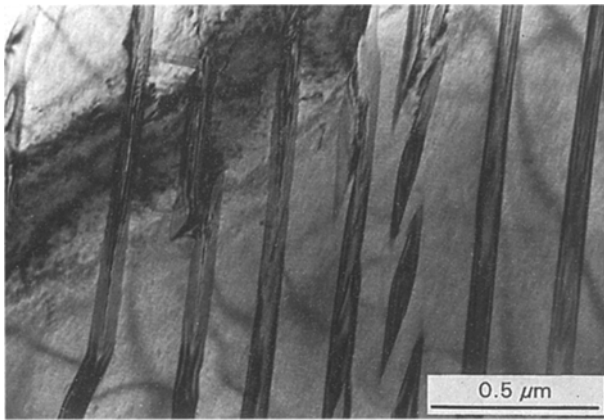


Figure 7 TEM aspect of the cells of discontinuous precipitation in the sample aged for 1 h at 800 °C.

austenitic matrix (Fig. 7). The plates of Cr_2N possess an hexagonal structure with the parameters $a = 0.418 \text{ nm}$ and $c = 0.444 \text{ nm}$. They obey the following orientation relationships with the austenite:

$$(\bar{1} 2 1) \text{Cr}_2\text{N} // (0 \bar{1} 0) \gamma$$

$$(1 1 \bar{1}) \text{Cr}_2\text{N} // (1 0 0) \gamma$$

$$(1 0 \bar{1}) \text{Cr}_2\text{N} // (3 \bar{1} \bar{1}) \gamma$$

The chemical composition of the particles of Cr_2N is $(\text{Cr}_{0.73}\text{Fe}_{0.17}\text{Mn}_{0.10})_2\text{N}$.

Moreover, the study by X-ray diffractometry of the samples aged at 800 °C, gives us further insights into their microstructural evolution with the duration of heat treatments. As illustrated by Fig. 8 for the particular case of the $(3 1 1) \gamma$ line, the diffraction peaks of austenite become splitting. This separation is related to the existence of two austenites with different lattice parameters. These two distinct austenites correspond to the untransformed matrix (γ) and to the interlamellar matrix (γ'), respectively. Table III displays the values (a_γ and $a_{\gamma'}$) of these parameters as well as the relative volume fraction of these two kinds of austenites. It is worth noting that a_γ decreases between 1 and 10 h of ageing, while $a_{\gamma'}$ remains constant during the whole duration of ageing at 800 °C. The evolution of the relative volume fractions of γ and γ'

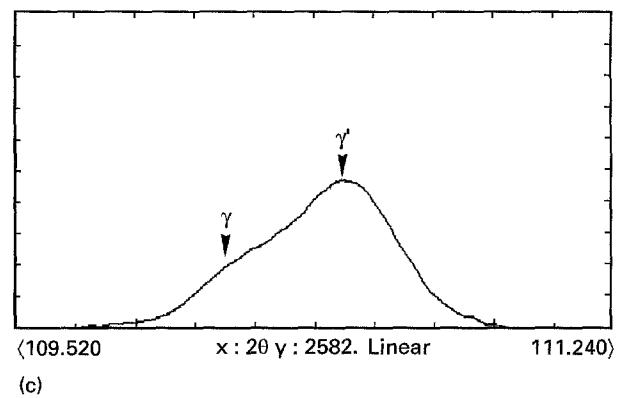
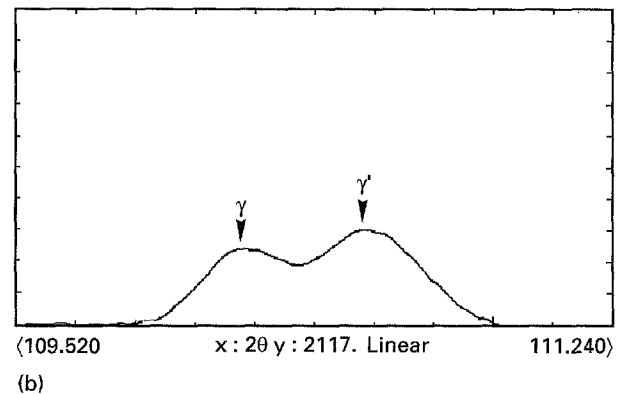
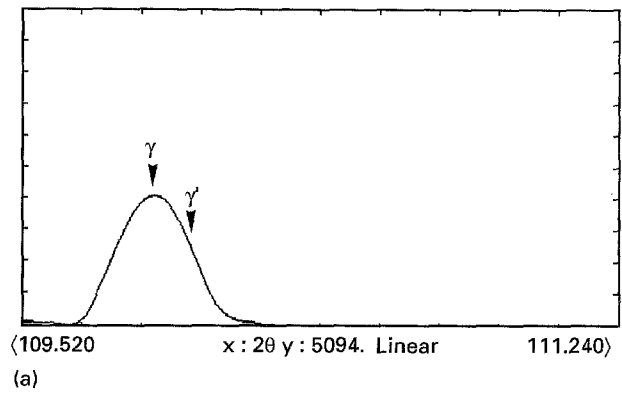
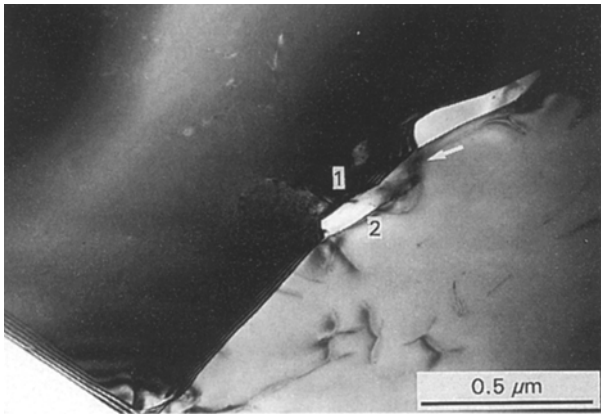


Figure 8 Effect of 800 °C ageing time on the $(3 1 1) \gamma$ X-ray diffraction peak. (a) 1 h; (b) 10 h; (c) 150 h.

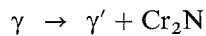
TABLE III Results of X-ray diffractometry with samples aged at 800 °C

Time (h)	a_γ (nm)	$a_{\gamma'}$ (nm)	% γ	% γ'
1	0.3622	0.3608	94	6
10	0.3616	0.3608	55	45
50	0.3616	0.3608	30	70
150	0.3616	0.3608	20	80

is very marked, and consistent with the previous measurements of the volume fraction of the cells of precipitation (Fig. 6). After 1 h of ageing, γ is the prevailing austenitic phase, because of the low volume fraction (8%) of the cells. On the contrary, after 150 h of treatment, γ' is the predominant phase, due to the major proportion (80%) of areas of discontinuous precipitation in the specimens.



To conclude, all these results correspond to the following scheme of the reaction of discontinuous precipitation



3.2. Nucleation stage

Fig. 2 shows that, in not prestrained materials, the precipitation of Cr_2N only occurs at grain boundaries, but never at coherent twin boundaries. This feature arises from the well known heterogeneous nucleation of Cr_2N [5]. Moreover, in accordance with this mechanism, Cr_2N precipitates on intragranular lattice defects in cold worked samples [5].

In the present case, the discontinuous precipitation of Cr_2N begins by the usual precipitation of plates of Cr_2N in the austenitic grain boundaries. A plate possesses a high energy interface (1) with the grain boundary, and a lower energy interface (2) with the grain in which it has formed (Fig. 9). Therefore, and as illustrated by Fig. 9, in order to decrease the internal energy of the material, the grain boundary moves along the interface (1) to substitute a piece of that interface (1) by a new and less energetic one between the plate and its original grain. The repetition of this motion of the grain boundary along adjacent plates, leads to the formation of the cells of discontinuous precipitation. To conclude with this mechanism of nucleation, it is important to note that it possesses the same driving force as the “pucker mechanism” of Tu and Turnbull [20, 21]. However, it differs from this latter reaction by the previous, but not subsequent, formation of plates of precipitates. In addition, it must be underlined that micrographs illustrating a nucleation stage in progress for a phenomenon of discontinuous precipitation are very scarce [19].

3.3. Growth stage

3.3.1. Reminder of usual theories

As a rule, the grain boundary discontinuous precipitation leads to the formation and growth of a two-phase lamellar structure behind a moving grain-boundary [19]. The combination of heterogeneous intergranular precipitation and concurrent migration of the grain

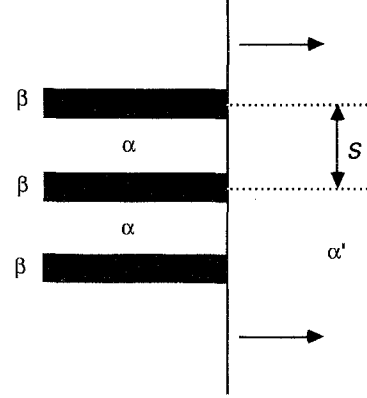


Figure 10 Schematic diagram showing idealized morphology of discontinuous reaction.

boundary is a complex phenomenon whose study has given rise to several models of isothermal kinetics of growth [19, 22].

The ideal isothermal features of the reactions of discontinuous precipitation, that formed the bases of the primary theories, are (1) an approximately planar front of precipitation, and (2) a constant interlamellar spacing (Fig. 10 [19]).

The relationship between the velocity of the moving grain boundary (G) and the interlamellar spacing (S) depends on the nature of the rate controlling diffusion phenomenon. In the case of growth governed by lattice diffusion, Zener has derived the following expression (Equation 1) for G [23]

$$G = \frac{K_1 D_v}{S} \quad (1)$$

where D_v is the volume diffusion coefficient of solute and K_1 is a constant which comprises the chemical compositions of the phases involved in the reaction of precipitation. This expression was calculated assuming that the same mechanism governs the eutectoid and the grain boundary discontinuous reactions and that all the free energy available for the precipitation is used for creating the interfaces between the precipitates and the matrix.

For the case of reactions controlled by the diffusion of a solute along grain boundaries, most theories derive from the model of Turnbull [24]. This theory predicts

$$G = \frac{K_2 D_B \delta}{S^2} \quad (2)$$

where D_B is the coefficient of diffusion along the grain boundary, δ is the boundary “thickness” along which the solute atoms can diffuse rapidly, and K_2 is a coefficient which, like K_1 depends on the compositions of the phases.

In this respect, it should be noticed that for the two rate controlling mechanisms, the compositions of the various phases are assumed constant during the reaction. Therefore, according to Equations 1 and 2, G must remain constant during isothermal ageing, because of the invariance of S and K_i ($i = 1$ or 2). The next section deals in particular with the two important parameters G and S .

3.3.2. Experimental features

In the present case, the growth of the discontinuous precipitation of Cr_2N is only studied at 800°C . This restriction is explained by the result of 1 h ageing treatments which show that both the size and the volume fraction of the cells of precipitation reach a maximum at 800°C . The accuracy of measurements increases indeed with the size of the cells.

Figs 11 and 12 display the evolutions of the two parameters G and S with ageing time at 800°C . The migration rate of the advancing interface G decreases, while the interlamellar spacing S increases in these isothermal conditions. It is worth noting that these variations of G and S in isothermal conditions contradict the predictions of usual theories. In order to investigate this discrepancy between theory and experiment, the behaviour of the interstitial element is considered. In fact, the usual theories deal only with binary substitutional alloys.

The average nitrogen contents, in both the untransformed austenitic matrix and the interlamellar austenitic layers, are deduced from the measurements of lattice parameters by XRD, and from the dependence of these lattice parameters on the content of nitrogen in solid solution for 19% Mn, 19% Cr austenitic steels (Fig. 13 [3]).

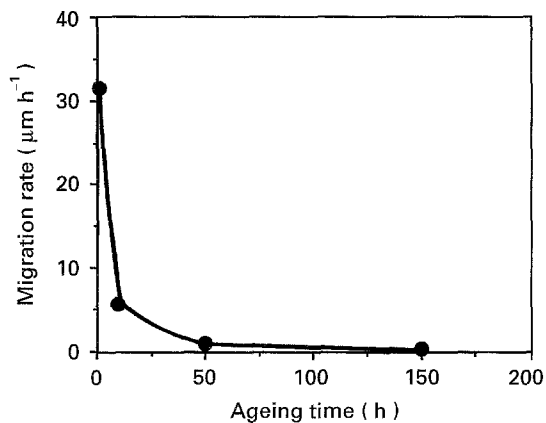


Figure 11 Effect of 800°C ageing time on the kinetics of growth.

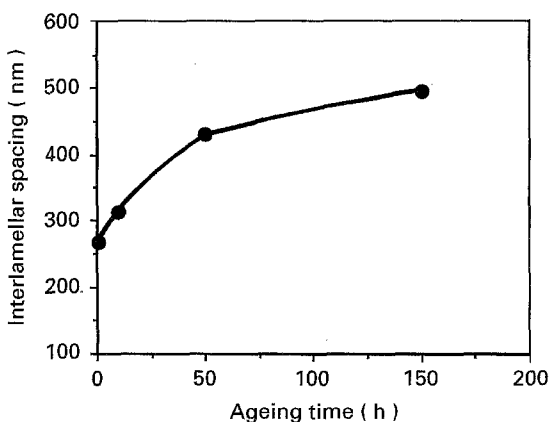


Figure 12 Increase of interlamellar spacing with ageing time at 800°C .

Fig. 14 shows that, as revealed by the decrease of the lattice parameter of the γ austenite, the nitrogen content of the austenitic matrix decreases between 1 and 10 h of ageing at 800°C . In consequence, the

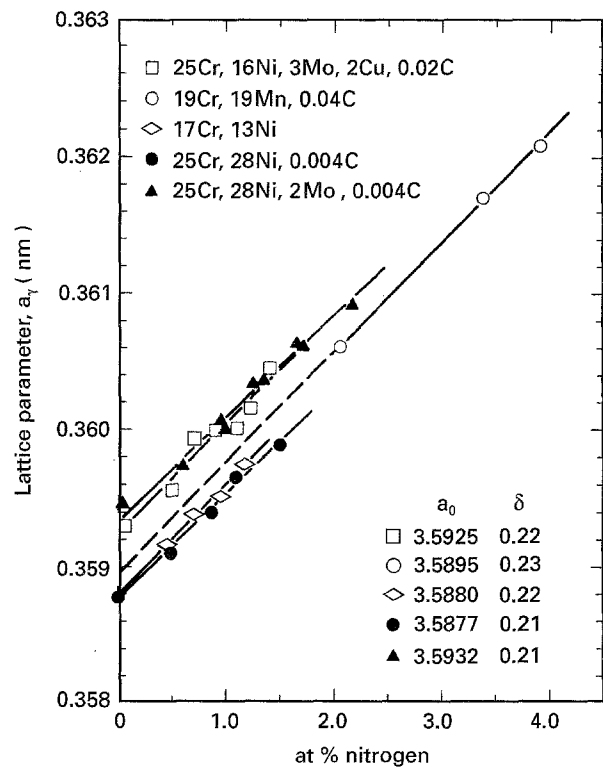


Figure 13 Crystal lattice parameter of austenitic stainless steels as a function of nitrogen concentration.

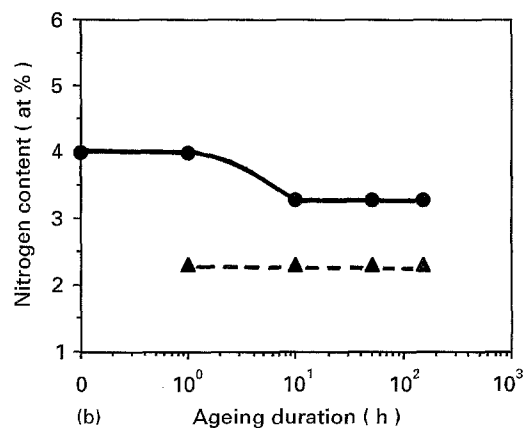
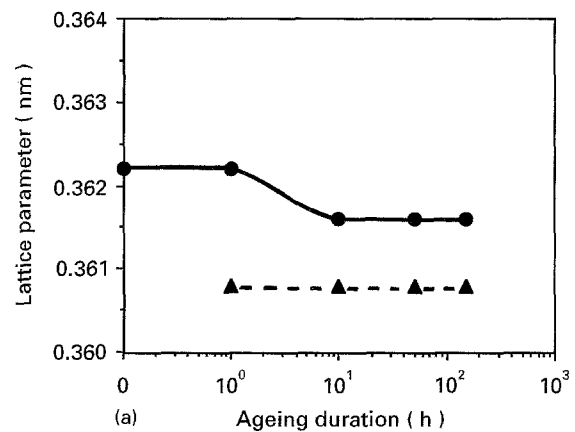


Figure 14 Effect of ageing time at 800°C on (a) the lattice parameter and on (b) the nitrogen content of the austenites. ● untransformed matrix; ▲ interlamellar matrix.

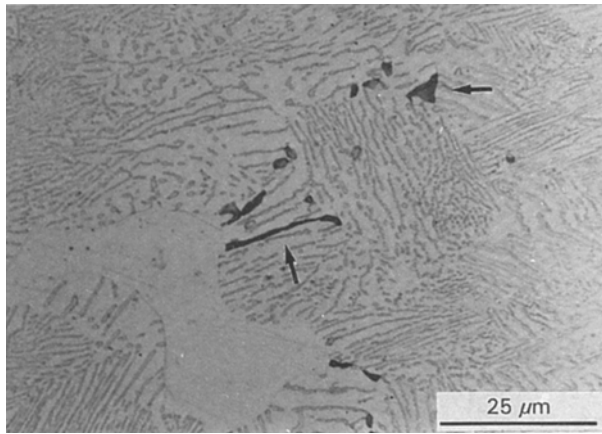


Figure 15 Precipitation state in a sample aged for 50 hours at 800°C.

nitrogen content does not remain invariant in the untransformed matrix, far ahead of the moving cell boundary. This fact is very astonishing because it is generally admitted that, in the course of discontinuous precipitation, the concentration of solute varies only at the front of reaction. On the contrary, the average nitrogen concentration of the interlamellar austenitic layers (γ') remains at a constant level during the whole duration of the phenomenon of precipitation. This observation implies that the austenite of the precipitation cells has a nitrogen content in equilibrium with Cr_2N , at least at the interfaces between the two phases in the cells.

3.4. Precipitation of sigma phase during ageing at 800°C

Beside the precipitation of Cr_2N , the samples aged for 50 h or more at 800°C, display massive particles (arrowed on Fig. 15). From the literature data [25], these precipitates were identified as sigma phase. Indeed, they possess both a tetragonal structure with the following parameters $a = b = 0.8800$ nm and $c = 0.4544$ nm, and a chemical composition of $\text{Fe}_{0.50}\text{Cr}_{0.33}\text{Mn}_{0.17}$, established by EDX measurements. The volume fraction of this intermetallic compound increases with ageing time, and this evolution suggests an incubation time of about 10 h [26]. Moreover, Fig. 15 shows that the sigma phase forms exclusively in the cell boundary of discontinuous precipitation of Cr_2N .

3.5. Mechanical behaviour of aged samples

Fig. 16 displays the evolution of the hardness with the one hour ageing temperature. The hardness of the sample in the as-quenched state is very high for an austenitic steel [27].

The alloy presents a slight strengthening after ageing at 800°C. The actuality of this hardening is confirmed by the prolongation of the 800°C thermal treatment (Fig. 17). It is observed that the hardness increases noticeably during the first ten hours of ageing, before remaining at a high level close to 300 H_v for the samples aged from 10 to 150 h.

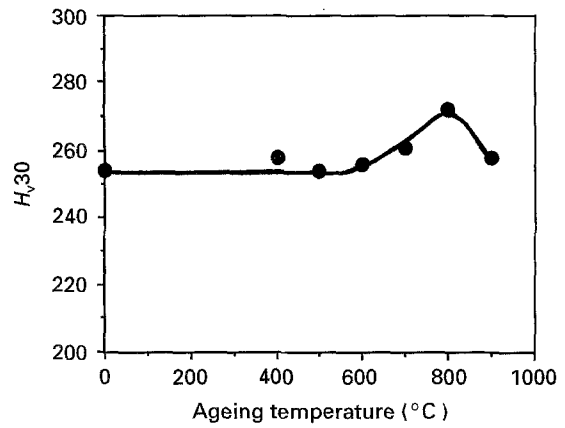


Figure 16 Effect of 1 h ageing temperature on hardness.

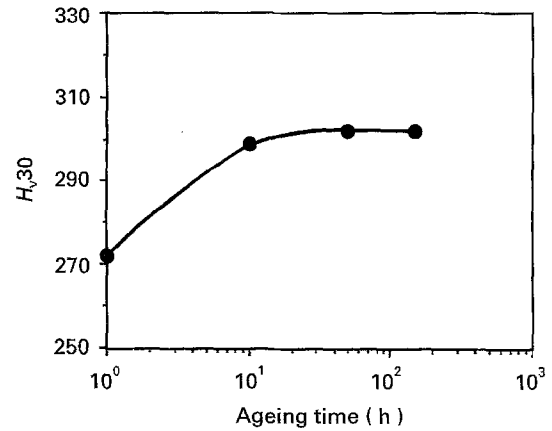


Figure 17 800°C ageing curve.

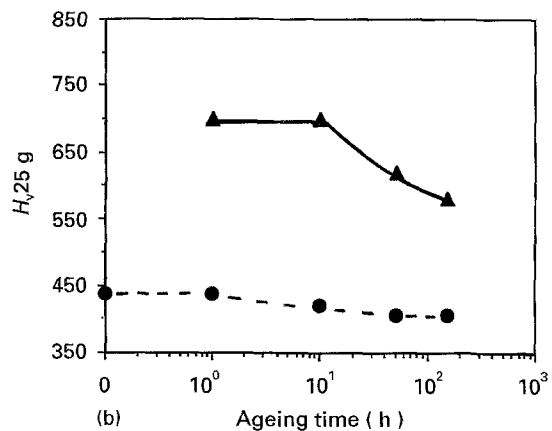
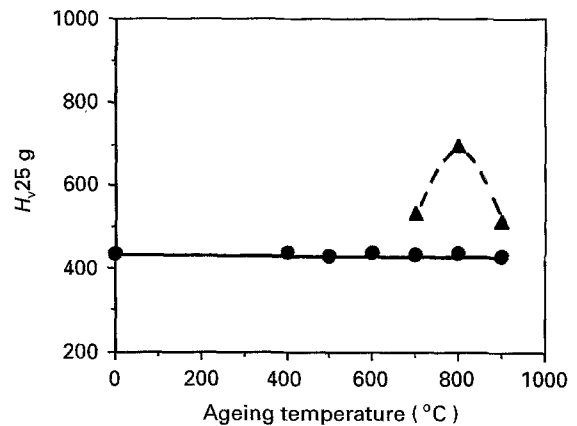


Figure 18 (a) Effect of ageing temperature on the microhardness of the matrix and of the precipitation cells. (b) 800°C ageing curves of the matrix and precipitation cells. ● untransformed matrix; ▲ precipitation cells.

The comparison between the evolutions of both the hardness and the microstructure of the samples, ascribes the strengthening of the steel to the effect of the discontinuous precipitation of Cr_2N . This conclusion arises from the following observations. On the one hand, the outset of the hardening coincides with the beginning of the reaction of discontinuous precipitation. On the other hand, the more important the volume fraction of cells, the higher is the level of hardness. Furthermore, microhardness measurements (under a load of 25 g) carried out in the untransformed matrix and in the discontinuous precipitation cells are presented in Fig. 18(a) and (b). Several facts can be established from these curves:

1. The specific hardness of the cells is higher than the hardness of the austenitic matrix.
2. After one hour ageing the hardness of the untransformed matrix remains constant (Fig. 18(a)). On the contrary, it decreases with the prolongation of the thermal treatment at 800°C (Fig. 18(b)).

4. Discussion

4.1. Mechanism of precipitation growth

This investigation of the growth stage of the discontinuous precipitation of Cr_2N shows that there is a discrepancy between the experimental observations and the growth features described by usual models. In this paragraph, we shall try to explain in a qualitative way, the cause of these differences. Above all, it should be noticed that the mechanism of growth of the present reaction is much more complex than the hypothesis of the usual theories, i.e. a reaction governed by the only grain boundary diffusion of a single substitutional element. Indeed, the present reaction involves two diffusion mechanisms, the diffusion of both an interstitial solute, nitrogen, and a substitutional one, chromium [28]. First of all, the redistribution of solutes during ageing will be considered. Then, the effect of this feature on the decrease of the migration rate of the cell boundary, as well as on the incomplete character of the reaction of precipitation will be discussed, and explained.

The decrease of the nitrogen content in the untransformed matrix, points out the actuality of a lattice diffusion of nitrogen from supersaturated austenite to precipitation cells. This deduction is in good agreement with both the high diffusivity of interstitial nitrogen at the temperature of ageing (800°C), and the increase with ageing time of the average nitrogen content of the domains of discontinuous precipitation (Fig. 19). The time required by a nitrogen atom to diffuse through a grain of the austenitic matrix is close to 1.6×10^4 s, i.e. 4 h and 30 min. This estimation arises from the use of the coefficient of bulk diffusion of nitrogen in Cr–Ni austenitic stainless steels ($4 \times 10^{-3} \text{ m}^2 \text{ s}^{-1}$ at 800°C [29]). Moreover it is worth noting that this period is of the same order of magnitude as that of the nitrogen impoverishment in the untransformed matrix (Fig. 14(b)).

In addition, and due to the rapid diffusion of interstitial nitrogen, it is reasonable to think that the kinetics

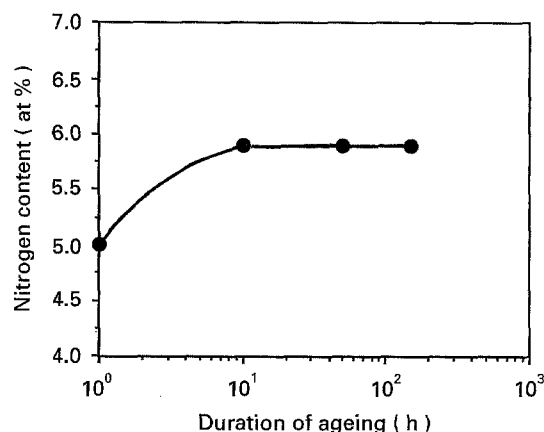


Figure 19 Effect of ageing time at 800°C on the average nitrogen content of the cells.

of growth of the discontinuous precipitation of Cr_2N is controlled by the far slower grain boundary diffusion of chromium. With this assumption, the average migration rate of the moving cell boundary G is related to the interlamellar spacing S , by the following equations [29]

$$G = \frac{D_{\text{Cr}}^{\text{v}}}{S} \quad (3)$$

for a growth governed by the volume diffusion of chromium, whereas

$$G = \frac{4 \delta D_{\text{Cr}}^{\text{gb}}}{S^2} \quad (4)$$

for a reaction controlled by the intergranular diffusion of chromium.

In these relations, D_{Cr}^{v} and $D_{\text{Cr}}^{\text{gb}}$ are the lattice and grain boundary diffusion coefficients of chromium respectively, S is the interlamellar spacing and δ is the thickness of the moving cell/matrix interface. These two kinetics are estimated in a rough way by assuming that the diffusivity of chromium does not differ between Cr–Mn and Cr–Ni steels. Indeed, the coefficients of diffusion have only been measured in Cr–Ni austenitic stainless steels ($D_{\text{Cr}}^{\text{v}} = 2 \times 10^{-18} \text{ m}^2 \text{ s}^{-1}$ [30] and $\delta D_{\text{Cr}}^{\text{gb}} = 4 \times 10^{-23} \text{ m}^3 \text{ s}^{-1}$ [31]). The results are presented in Fig. 20 which compares the theoretical

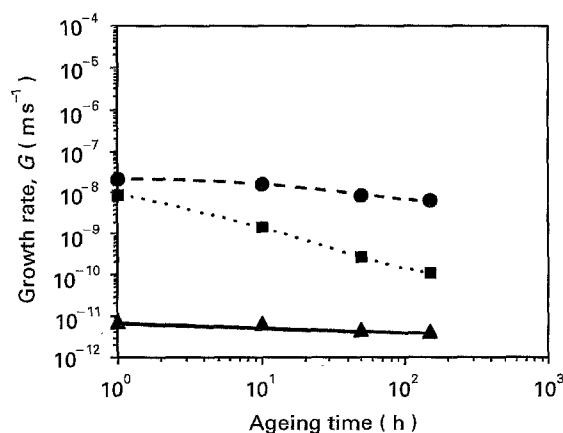


Figure 20 The mechanism of growth of discontinuous precipitation changes during ageing at 800°C . ■ experimental; ▲ volume diffusion; ● grain boundary diffusion.

and effective growth rates during the 800 °C thermal treatment. In the early stages of ageing, of up to 10 h, the kinetics of growth is very close to its estimate with the hypothesis of its control by the intergranular diffusion of chromium. At later stages of ageing, the experimental growth rate tends more and more towards its theoretical estimate for a reaction governed by volume diffusion. These observations suggest that the precipitation growth occurs in non-steady state conditions. The growth rate is successively controlled by the grain boundary and then by the lattice diffusion of chromium. Similar results have already been published with Fe–Ni–N austenitic stainless steels [29].

The velocity of the moving boundary of the cells of discontinuous precipitation, is mainly determined by the degree of nitrogen supersaturation in the austenitic matrix [29]. In the early stages of the reaction, nitrogen flows very fast from supersaturated austenite to precipitation domains via a long-range volume diffusion mechanism. This phenomenon induces a decrease of the nitrogen supersaturation with the consequence of a reduction of the driving force of the reaction. So the deceleration of the displacement of the moving cell boundary becomes explainable. According to this argument, the migration should proceed until the nitrogen supersaturation becomes equal to zero. Consequently, this interpretation can not explain why, experimentally, the growth stops in spite of a remaining and substantial nitrogen supersaturation in the untransformed matrix. This supersaturation is obvious in Fig. 14(b) which shows a 3 at % concentration of nitrogen in the untransformed matrix at long ageing

times. As a matter of fact, this concentration exceeds clearly the 0.8 at % value for the limit of solubility of nitrogen in the present alloy. This latter estimate is deduced from the 0.72 at % solubility limit of nitrogen in 25Cr–20Ni steels [29, 32], and taking account of the small increase of the solubility of nitrogen in presence of manganese [33].

Moreover, Fig. 21 displays a border of preferential etching along and ahead of the moving cell boundaries. This feature suggests the existence of a chromium depleted diffusion zone ahead of the precipitation front. This impoverishment agrees well with the effectiveness of the lattice diffusion of chromium to control the kinetics of growth at long ageing times. In accordance with this mechanism, the decrease of the nitrogen supersaturation in the untransformed matrix gives rise to a loss of the chemical driving force for the discontinuous precipitation, with the consequence of a diminution of the migration rate. This slowing down is further enhanced by the widening of the chromium impoverished diffusion zone that reduces the kinetics of the diffusion of chromium at long ageing times. This widening explains the incompleteness of the discontinuous precipitation of Cr₂N, though the driving force is not equal to zero because of the remaining nitrogen supersaturation of the matrix.

To summarize, it is obvious that the present reaction of discontinuous precipitation does not occur in steady state conditions, by the only intergranular diffusion of a substitutional element. Therefore it is not surprising that it does not satisfy the provisions of the usual theories. To fulfil this lack of theory, a model of

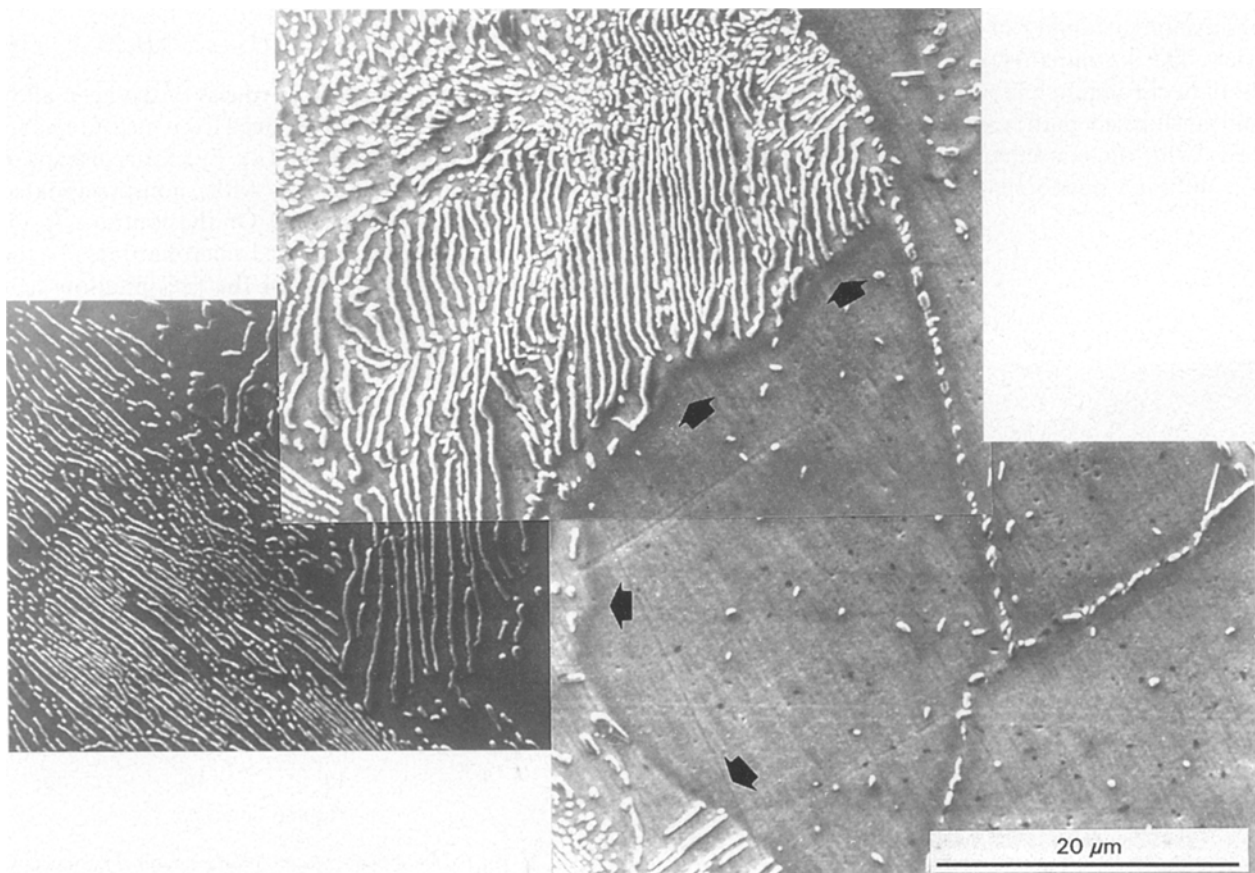


Figure 21 Preferential etching at the border of the precipitation cells after 150 h of ageing at 800 °C.

growth that takes account of the non-steady state character of the reaction and therefore of the chronology of the successive rate controlling phenomena has recently been published [34].

4.2. Existence of sigma phase

The cell boundary localization of sigma phase agrees well with its well known heterogeneous nucleation, which requires high energy interfaces. In contrast, the mechanism of growth of sigma phase is less obvious. The two following explanations would require further investigations.

First, and as illustrated by Fig. 22 that displays a thickening of the particles of sigma in contact with the plates of Cr_2N , sigma seems to precipitate at the expense of Cr_2N . However, this mechanism is not *a priori* favoured by the local chemical composition (local enrichments in chromium and in nitrogen) arising from the dissolution of Cr_2N . As a matter of fact, it is well known that nitrogen in solid solution is not convenient for the nucleation of sigma [35]. In accordance with this consideration, the formation of sigma can only be explained by a thermodynamic stability higher than that of Cr_2N . Moreover, it is relevant to note that this explanation is strengthened by the increase of the stability of sigma with the manganese content [35].

Secondly, and in contradiction with the previous interpretation of Fig. 22, the irregularity of the interface of the sigma phase may result merely from the primary morphology of the cell boundary. With this assumption, the formation of sigma in the front of precipitation should result from both the higher thermodynamic stability of sigma and a kinetic point of view. The accompanying variations of concentrations both in chromium and nitrogen would be lower in the untransformed matrix than in the two parts of the cells, with the consequence of a smaller duration for the diffusion phenomena.

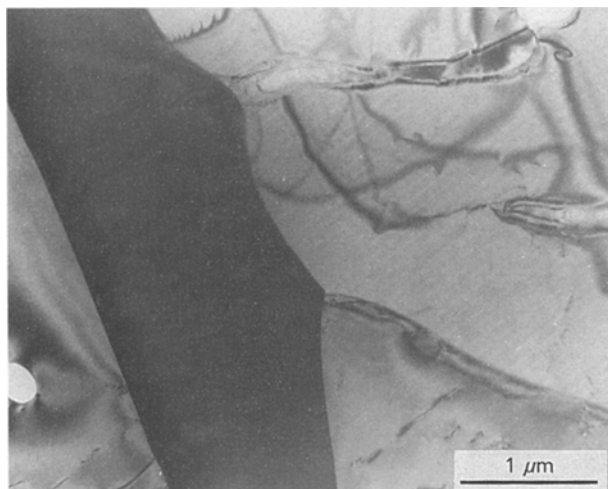


Figure 22 Morphology of sigma phase at a cell boundary in a sample aged for 150 h at 800 °C.

4.3. Mechanical behaviour of aged samples

As a rule the strength of high nitrogen austenitic steels is governed by the level of nitrogen in solid solution [3]. On the contrary, the effect of the discontinuous precipitation of Cr_2N on the mechanical behaviour is debatable at the moment [2, 36]. However, a precipitation hardening phenomenon occurs in the present case.

In accordance with the first result, and whatever the temperature of one hour ageing, the hardness of the untransformed matrix (γ) remains constant (Fig. 18(a)) because of the invariance of the nitrogen content in solid solution [28]. Moreover, the decrease of the γ hardness for holding times longer than one hour at 800 °C is consistent with the impoverishment of nitrogen in solid solution, due to the lattice diffusion of nitrogen from austenite to precipitation cells (Fig. 14(b)).

On the contrary, the diminution of hardness of the cells during isothermal ageing at 800 °C (Fig. 18(b)) can not be attributed to a modification of the nitrogen content in the interlamellar spacing, because it has already been verified that this concentration remains constant. It seems more judicious to allot this decrease of hardness to the increase of the spacing between the Cr_2N plates (Fig. 12). Otherwise, the comparison between the evolutions of hardness and microstructure of the aged samples attributes the strengthening of the alloy to the effect of the discontinuous precipitation of Cr_2N [28]. In addition, Fig. 23 proves that the microhardness of the samples agrees well with Equation 5. This additive law is similar to that of "ferrite-pearlitic" steels, which considers the volume fraction of the monophasic constituent to the 1/3 power [37]

$$H_{v,25} = f_{\gamma}^{1/3} H_{v,25_{\gamma}} + (1 - f_{\gamma}^{1/3}) H_{v,25_{\text{cells}}} \quad (5)$$

$H_{v,25}$ symbolizes the microhardness of the aged alloy under a load of 25 g. It is deduced from measurements of hardness under a load of 30 kg, by means of a law of correspondence established with non-precipitated samples ($H_{v,25} = 1.7 H_{v,30 \text{ kg}}$). On the contrary, $H_{v,25_{\gamma}}$ and $H_{v,25_{\text{cells}}}$ are the measured microhardness of the untransformed matrix and of the precipitation cells

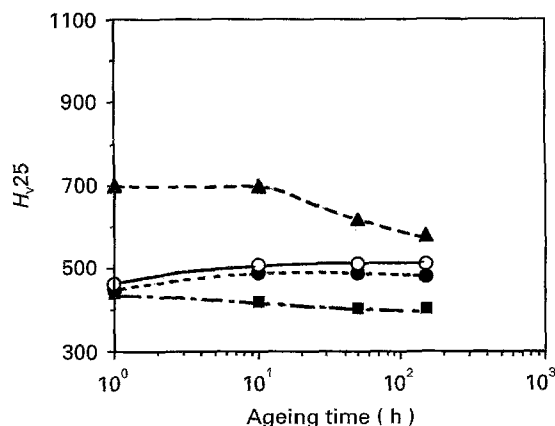


Figure 23 The hardness of the precipitation cells and of the untransformed matrix are additive. ■ untransformed matrix; ▲ precipitation cells; ● calculated hardness; ○ experimental hardness.

respectively. f_γ is the volume fraction of austenitic matrix.

Taking account of both the complexity and the multiplicity (presence of sigma phase) of the precipitation phenomena, and of the difficulty to describe the mechanical behaviour of duplex structures, the concordance between experimental and calculated points is very satisfactory. With regard to this mechanical behaviour, a more detailed description of precipitation hardening, founded on the study of the mechanisms of interactions between dislocations and plates of Cr_2N is now ongoing.

5. Conclusions

The reactions of precipitation in this 1 wt % nitrogen austenitic stainless steel are complex and exert a significant effect on the mechanical properties.

The nucleation of the discontinuous precipitation of Cr_2N is induced by the decrease of the energy of the interfaces of the primary intergranular plates of precipitates. The growth stage of this precipitation does not verify the assumptions and therefore, the expectations of usual models, because of its chemical complexity involving the diffusion of both an interstitial element and a substitutional one. The kinetics of growth is governed at first by the grain boundary and subsequently by the lattice diffusion of chromium.

An additional precipitation of sigma phase occurs quite rapidly during ageing at 800 °C. The mechanism of formation of this second phase needs more thorough studies. However, this formation of sigma phase suggests that the present alloy is not convenient for high temperature applications. In fact, the presence of several percents in volume fraction of the brittle sigma phase, from the first hours of ageing at 800 °C, is very damaging for the mechanical properties.

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