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Influence of the Quenching Rate on the Spinodal Decomposition in a Duplex Stainless Steel

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Abstract: Cast duplex stainless steels are known to be susceptible to embrittlement after long term ageing at intermediate temperatures (300-400°C). This embrittlement is related to the spinodal decomposition that occurs in the ferrite phase. Steels of equivalent composition after undergoing the seemingly same heat treatment exhibit different microstructural and mechanical evolutions. One of the assumptions which explains this is based on the influence of the quenching rate. For this purpose, a set of different cooling rates (2°C/s to 20°C/s) has been applied, and the resulting microstructure analysed. The atom probe was used because of its capability to investigate the fine-scale α - α' spinodal decomposition of the ferrite. It is shown that the quenching rate influences both the initial composition amplitude in unaged specimens and the rate of development of chromium concentration fluctuations in the aged ferrite.

1. INTRODUCTION

Cast duplex stainless steels with ferrite-austenite microstructure are extensively used in nuclear, oil and chemical industries because, in addition to high corrosion and cracking resistance, they show high-strength and excellent weldability for large components [1].

In the mid seventies, these steels have been shown to be susceptible to embrittlement after long term ageing at intermediate temperature, i.e. 300 to 400°C [2]. This embrittlement is characterised by an increase in hardness and a loss of impact toughness associated with a shift of the ductile to brittle transition temperature [3]. The mechanism responsible for this embrittlement has been identified as being the so-called "475°C embrittlement". Various techniques, amongst which is Atom Probe Field Ion Microscopy (APFIM), demonstrated that in the range 300-400°C, the ferritic solid solution decomposes into α (Fe-rich) and α' (Cr-rich) domains according to a spinodal process [4]. The resulting microstructure is a highly interconnected α - α' network that develops on a nanometre scale. Extensive atom probe studies demonstrated that this process is responsible for the embrittlement of stainless steels, whatever the austenite content is from 0 to at least 80%. In addition, the evolution of the ferrite hardness has been linearly correlated with the spinodal amplitude. Assuming a thermally activated process, numerous studies concluded in an activation energy in the range 300-400°C of about 230 kJ/mol, in good agreement with that of Cr diffusion in α -Fe.

If the main process responsible for embrittlement is clearly identified, many aspects affecting the rate of embrittlement remain unexplained. Indeed, large differences in the behaviour of cast duplex stainless steels and of single phase have been reported in the literature [5-7]. For example, Brown showed rates of hardening up to 50 times faster (with the same activation energy) for model Fe-26Cr-5Ni alloys when the homogenisation temperature was varied in the range 1250 to 1000°C [7]. This phenomenon was

associated with the disappearance of the austenite from the microstructure, although no explanation could be found for it. Schwartz and LaSalle also observed different spinodal decomposition rates for purely ferritic specimens that experienced different homogenisation temperatures (1200 and 850°C) [8]. From another point of view, Danoix noticed that unaged specimens taken from the bulk of an ingot exhibited a spinodal amplitude larger than that of the same specimen re-solution treated, but more rapidly quenched [5]. The same phenomenon has also been observed by Sassen [9]. In those two cases, the cooling rate was supposed to be responsible for the observed difference.

It appears that to identify the causes of those different behaviours during thermal ageing, the prior thermal history of the specimens analysed, i.e. the manufacturing, has to be taken into account. For duplex stainless steels, the consecutive manufacturing stages can be summarised as presented in figure 1.

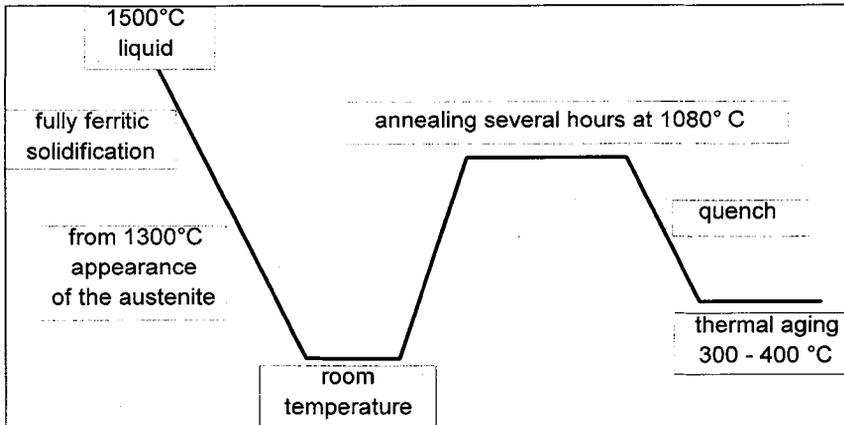


Figure 1: Manufacturing sequence of duplex stainless steel castings

The first stage is the solidification which, in the first step is purely ferritic. At this stage, the initial size and morphology of the ferrite grains is determined. Coarse equiaxed grains are observed in the core of large pieces, and fine grains, elongated in the direction of the temperature gradient during solidification at their surface. If γ -like element concentrations (mainly C and Ni) are sufficient, part of the primary δ ferrite transforms into γ austenite. The austenite appearance temperature is closely related to the α -forming over γ -forming element concentration ratio. The second step is the homogenisation treatment, the temperature of which may vary in the range 850 to 1300°C. The annealing temperature sets the ferrite/austenite ratio of the steel, and consequently the partitioning of the alloying element in both phases. For the duplex stainless steel under investigation, the homogenisation temperature was 1080°C, in order to form about 70% of austenite. The observations of Brown and Schwartz are most probably related to this step. The last stage is the quench of the annealed material. As previously mentioned, the quenching rate is suspected to be an important parameter influencing the initial mechanical properties and the ferrite microstructure of the material before thermal ageing.

The aim of this paper is to present initial results concerning the importance of the quenching rate.

2. MATERIALS

The samples studied have been supplied by Electricité de France, and their composition is given table 1. They were taken from a static cast, the thickness of which varies in the range 125 to 140 mm. Because of that thickness, the quenching rate is inhomogeneous within the cast. It has been estimated to be about 2 °C/s in the core (i.e. 60 to 70 mm in depth) and about 10 °C/s close to the surface. As a consequence, the position of each sample was carefully noted. Specimens under investigation referred to as « current zone » all originate at least 50 mm from the surface in each direction.

ELEMENTS	Cr	Ni	Mo	C	N	Si	Mn	Fe	Ferrite content
weight%	21.2	9.7	2.5	0.032	0.051	1.1	0.9	64.6	30%
atom%	22.0	8.9	1.4	0.14	0.2	2.0	0.9	64.5	30%

Table 1: Chemical composition and ferrite content of the studied duplex stainless steel as measured by electron microprobe

A thin (27 mm thick) sheet of metal was taken from this last region, and re-solution treated at 1080°C and then water quenched. These specimens will be referred to as « re-quenched » specimens. For this thickness the cooling rate was about 20°C/s.

3. EXPERIMENTAL

Atom probe analyses were performed on an energy-compensated instrument [10] at 40K with a pulse/standing voltage ratio of 20% in a vacuum better than $3 \cdot 10^{-8}$ Pa. Analysis direction was left random. In order to minimise and quantify the effects of spatial convolution between the analysis cylinder and the fine scale α - α' microstructure, analyses were carried out with a constant lateral resolution. The lateral resolution was kept constant at 1 nm using a variable iris diaphragm [11]. In order to maintain statistical fluctuations on an acceptable level, the composition of successive points on the concentration profiles are calculated over 50 atoms, corresponding to 1.2 nm in depth. At least 3 specimens were analysed for each heat treatment.

The extent of spinodal amplitude in the ferrite phase is quantified by the statistical distance (called variation, V) between experimental and binomial chromium concentration frequency distribution. Figure 2 shows a Cr concentration profile from the current zone aged 2500h at 350°C. On the right-hand side of the diagram, the corresponding experimental concentration frequency distribution and the difference between experimental and binomial distribution are represented.

This statistical distance is the integral area difference between the two distributions. Because these two distributions are normalised, V varies in the range 0 to 2. This parameter has been shown to be an appropriate estimate of the extend of spinodal amplitude, except when smaller than about 0.05-0.1. Indeed, because of the finite size of the experimental set of data, statistical fluctuation of that order are expected, and may affect the determination of V . Experimental values of V smaller than 0.1 should therefore be interpreted with care.

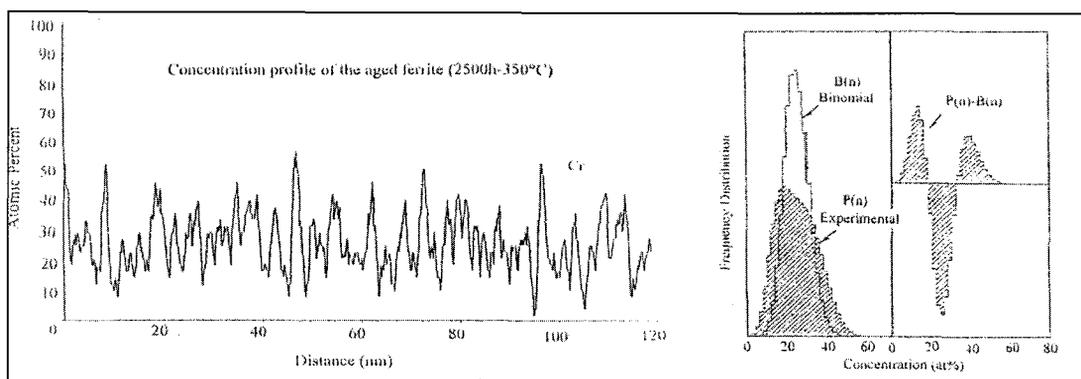


figure 2 : Derivation of the variation V from an experimental concentration profile

4. RESULTS AND DISCUSSIONS

4.1 Chromium concentration amplitude as a function of specimen extraction depth

Samples coming from different depths have been analysed in the unaged condition and after ageing 30,000 h at 300°C. The cooling rate has been estimated to be about 10°C/s for the surface sample and about 2°C/s in the core of the elbow. The results of atom probe analyses are presented in table 2.

current zone depth (mm)	quenching rate (°C/s)	unaged (V)	aged 30,000 h @ 300°C (V)
1	approx. 10	0.05	0.05
12	between 2 and 10	Not determined	0.18
60 (core)	approx. 2	0.19	0.27

table 2: Variation V as a function of the extraction depth and of the ageing treatment

Two important results can be derived from these data. First of all, in the unaged condition, the specimen from the core exhibits significant concentration amplitude, whereas weak (or none) is detected from the surface specimen. The second important result concerns the amplitude of fluctuations developed in both specimens after ageing 30,000 h at 300°C. No significant evolution is observed for the surface specimen, whereas an increase of 0.08 occurs for the one of the core. From a mechanical point of view, these differences are associated with an important loss of impact toughness for the core specimen aged 30,000 h at 300°C. Two fabrication parameters differ in both areas. The first is the microstructure resulting from solidification: in the core, coarse equiaxe grains are observed, which become elongated closer to the surface. This difference cannot directly explain either the Cr-concentration fluctuation in the « as received » conditions, or the difference in the development of fluctuations during thermal ageing. The second difference is the cooling rate experienced in each zone (10 vs. 2°C/s), which is more likely to be responsible for the observed differences.

In order to assess the influence of the quenching rate, and to eliminate a possible effect of the initial microstructure of the specimens, a second set of samples was analysed.

4.2 Influence of the quenching rate

In order to point out the only effect of the cooling rate, a thin plate of material has been taken from the current zone in the centre of the cast and re-solution treated at the same homogenisation temperature (1080°C), and then water quenched. These specimens are referred to as « re-quenched » specimens. The quenching rate for this thin plate has been estimated to be 20°C/s. Specimens were aged at different temperatures and analysed by atom-probe. Results are compared with those obtained from specimens originating from the same area, but which did not receive the re-homogenisation treatment. These latter specimens will be referred to as « as received » specimens, even when they are subsequently thermally aged. The related values of V are presented in table 3. Many conclusions can be drawn from these data.

ageing treatment	current zone « as received » $V_q=2^\circ\text{C/s}$	current zone « re-quenched » $V_q=20^\circ\text{C/s}$
unaged	$V_2 = 0.19$	$V_{20} = 0.05$
2500h-300°C	$V_2 = 0.06$	$V_{20} = 0.07$
2500h-325°C	$V_2 = 0.24$	$V_{20} = 0.08$
2500h-350°C	$V_2 = 0.58$	$V_{20} = 0.25$
2500h-400°C	$V_2 = 1.01$	$V_{20} = 0.98$

Table 3 : Evolution of the variation for « as received » and « re-quenched » specimen as a function of the ageing temperature

4.2.1 Unaged specimen

The unaged « requenched » specimen exhibits a low V value, identical to that measured on the unaged specimen taken from the skin of the current zone. Both specimens experienced rather high quenching rates ($>10^{\circ}\text{C/s}$), but have different ferrite solidification morphologies (resp. equiaxed and elongated ferrite grains). This result proves that this parameter cannot be regarded as responsible for the difference between the specimen analysed in the previous section. As a consequence, it is confirmed that the quenching rate is a key parameter for the estimation of the concentration amplitude in the unaged conditions.

4.2.2 « As received » specimen

First of all, a singular point is observed after ageing at 300°C . The concentration amplitude for this treatment is shown to be smaller than the one observed on the corresponding unaged specimen. This indicates a re-homogenisation of the decomposed Fe-Cr solid solution. This phenomenon has already been observed, but only for annealing temperatures in the range $550\text{--}600^{\circ}\text{C}$, i.e. above the Fe-Cr miscibility gap [12]. After ageing at 300°C , no such behaviour is expected as this temperature is well below the miscibility gap. Phase separation is expected to occur at this temperature, leading to V values larger than the one measured in the unaged specimen. At the moment, this result is not considered as reliable. Sample inversion is suspected, and a new set of specimens is under investigation in order to clarify this point. We will therefore not take into account this result in the course of this work. Concerning the evolution of V with ageing temperature, it is very similar to that observed on steel A10, a closely related duplex stainless steel we extensively analysed by Atom Probe [5].

4.2.3 « Requenché » specimen

V values remain very low after ageing at 300 and 325°C . Only a marginal evolution is observed. It is not certain that it is meaningful, although it indicates a slight increase of the concentration amplitude with increasing ageing temperature, as expected from the spinodal decomposition theory. It is only after ageing at 350°C that concentration fluctuations are unambiguously detected.

4.2.4 Comparison between « as received » and « requenché » specimen

We represented the evolution of $\Delta V = V_2 - V_{20}$ after ageing at various temperatures (figure 3). Even though this value has no obvious physical meaning, it is an easy way to point out the differences in the spinodal decomposition rates between both sets of samples. The positive initial ΔV value indicates the higher concentration amplitude in the « as received » conditions (cf. § 4-2-1). ΔV increase with increasing temperature up to 350°C shows that the rate of spinodal decomposition is larger for « as received » specimens than for « requenché » ones. So, not only the initial spinodal amplitude, but also the rate of development of spinodal amplitude is strongly dependent on the quenching rate. After pronounced ageing conditions (2500h @ 400°C), both specimens exhibit similar spinodal amplitudes. From a mechanical point of view, both specimens also exhibit the same low impact toughness, already situated on the lower shelf of the ductile to brittle transition curve. It is therefore clear that the final stages of decomposition are fairly similar, and are not influenced by the quenching rate.

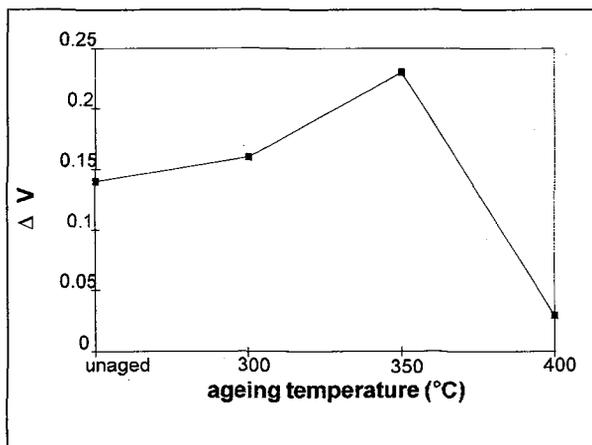


Figure 3 : Evolution of ΔV after ageing 2,500 h at various temperatures

5. CONCLUSION

This work has shown that the quenching rate of large pieces made of cast duplex stainless steel has a major influence on the spinodal decomposition which occurs in the ferrite phase during thermal ageing at temperatures in the range 300-400°C. Indeed, it has been shown that the initial concentration amplitude observed in unaged specimen, as well as the rate of development of spinodal concentration fluctuations, increase with decreasing quenching rates. In addition, it has been shown that the morphology of the solidification primary ferrite grains has no influence on the initial concentration amplitude of the ferrite phase.

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