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The effect of deformation on the sigma phase occurrence in some stainless steels

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Abstract

The effect of deformation on sigma phase occurrence has been studied in two stainless steels, a duplex stainless steel and a ferritic stainless steel. The samples were deformed by rolling at –70^{0}C and –196^{0}C and subsequently annealed at 700^{0}C for up to 48 hours. Results show that the $\alpha \rightarrow \gamma_2$ reaction precedes the sluggish sigma (σ) phase occurrence. However γ_2 latter becomes enveloped by σ and the growth of the former is inhibited. The effect of deformation is increased rate of $\alpha \rightarrow \gamma_2$ reaction. This results in more sites for the σ precipitation; σ precipitates at α/γ_2 and α/α boundaries. The effect of deformation therefore is to increase the rate of occurrence of σ.

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1.0 Introduction

The duplex (austenite + ferrite) steels are *Fe-Cr-Ni* alloys. They provide a favourable combination of the properties exhibited by the single-phase austenitic (γ) and ferritic (α) alloys with respect to corrosion resistance and mechanical properties [1-3].

These advantages notwithstanding, duplex stainless steels are susceptible to precipitation of other phases during solidification of the alloy, subsequent heat treatments, welding and other processes [4]. One such phase is the sigma phase first detected in 1927 [5]. The sigma phase is an intermetallic compound, rich in *Cr* and M_0, with tetragonal structure and non-magnetic [5,6]. It is hard and brittle and its occurrence also has deleterious effect on corrosion resistance [7-10]. The mechanism, times and temperature range of occurrence of the sigma phase have been reported widely [6,11-13]. Not much work has been done concerning the effect of deformation.

The present work is on the kinetics of the sigma phase occurrence during the annealing, essentially, of previously cold-worked materials.

2.0 Experimental procedure

The composition of the duplex and ferritic alloys are shown in Table 1 below:

Table 1: Alloy compositions (*wt*%)

	C	Cr	Ni	Mn	Si	M_0	Cu	S	P
Duplex alloy	0.026	20.60	6.62	1.60	0.46	2.45	1.64	0.018	0.031
Ferritic alloy	0.002	24.35	6.25	0.61	0.5	3.0	1.43	0.004	0.008

The alloys were supplied as 4mm thick plates. Samples about 20*mm* x 5*mm* x 4*mm* were cut from the materials and solution treated for one hour at 1050^{0}C and 1300^{0}C respectively for the Duplex and ferrific alloys. This was followed by water quenching.

These samples were then cold-rolled to 20 and 80% reduction at –196^{0}C. For the sub-zero temperature bath of liquid nitrogen was used. The samples were then annealed at 700^{0}C for up to 48-hours.

For transmission electron microscopy 3*mm* discs were thinned electrolytically in 10% perchloric acid in ethanol at 12*V*, 0.5*amp* and ice water temperature. Changes in ferromagnetic content were determined using a Suchsmith magnetic balance [14].

3.0 Results and discussion

The changes in ferromagnetic content of the alloys as a function of time of annealing at 700^0C is summarized in Table 2 below.

Table 2:

log *t* (min)	Duplex (20% reduction)	Ferritic (20% reduction)	Ferritic (80% reduction
0	45	100	100
0.5	35.5	89	83
1	32.5	65.5	55.5
1.5	32	55.5	27.5
2	26	41	14.5
2.5	20	16.5	8
3	9	6.5	0.3
3.5	4.5	3	0.1

For all the alloys the ferromagnetic content decreases with time. The decrease is expectedly fastest for the heavily deformed (80% reduction) condition of the ferritic alloy. The possible reactions that would account for the decrease are:

(a) reversal of the deformation-induced martensite (α^1) to austenite (γ) i.e. ($\alpha^1 \rightarrow \gamma$).
α' is magnetic, γ is non-magnetic. This reaction would occur only in the duplex alloy.

(b) ferrite (α) $\rightarrow$ austenite (γ_2). α is magnetic, γ_2 is non-magnetic.

(c) precipitation of the sigma phase (σ). σ is non-magnetic.

However structural evidence shows that in these times of annealing the α' laths have only largely recovered (plate 1). This rules out α'-γ reaction making any significant contribution.

Concerning γ_2, some precipitation of this phase occurs earlier, in ~3 minutes annealing of 80% deformed ferritic alloy. At longer times σ precipitation becomes evident (plate 2). Extensive growth of the σ phase is observed and the previously formed γ_2 precipitates are surrounded. The α-matrix is largely consumed. The implication of this is that the growth, with time, of γ_2 is inhibited by the occurrence of σ. Therefore any complications of the kinetics of the σ phase occurrence by γ_2 formation and $\alpha' \rightarrow \gamma$ reaction are minimal.

The Johnson-Mehl [15] equation can be applied in the study of the kinetics of the occurrence of the σ phase. The generalized equation, relating to the isothermal kinetics of transformation in metals is given as:

$$X = l - e^{-(kt)^n} \qquad (3.1)$$

where X = fraction (of α in the present work) transformed in time t.
n and k = time exponent and rate constants respectively.

This equation has been applied in the treatment of diffusion-controlled precipitations, and shown to closely approximate the time-dependence of precipitations for a considerable fraction of the reaction time [16,17].

This equation yields:

$$log \; log \left(\frac{1}{1-X}\right) = n \, log \, t + n \, log \, k - log \, 2.3 \qquad (3.2)$$

If the reaction conforms to the Johnson-Mehl equation, a graph of $log \, log \left(\frac{1}{1-X}\right) \; vs \; log \, t$ is linear. The graphs for the duplex alloy (previously deformed to 20% reduction) and the ferritic alloy deformed to 20 and 80% reduction) are presented in Figure 1. Considerable scatter of the points is noted, possibly due to complications arising from the $\alpha \rightarrow \gamma_2$ and any $\alpha' \rightarrow \gamma$ reactions. This have already been referred to and considered minimal. However linear portions may be observed for appreciable intervals of time.

Values of k obtained for some portions of Figure 1 are presented in Table 3.

Table 3: Rate constant (k) for portions in Graph 1

Alloy/Portion of graph	Rate values k(min^{-1})
Duplex (20% deformation)/A_1	2.25 x 10^{-3}
Ferritic (20% deformation)/B_1	1.35 x 10^{-2}
Ferritic (20% deformation)/B_2	8.39 x 10^{-3}
Ferritic (80% deformation)/C_1	3.37 x 10^{-2}
Ferritic (80% deformation)/C_2	1.28 x 10^{-1}

The *k*-values found in the present work are some orders of magnitude greater than those reported by Beetge

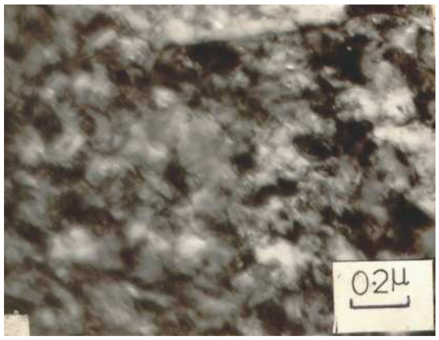


Plate 1: Extensive recovery in the original α' -laths of the duplex alloy

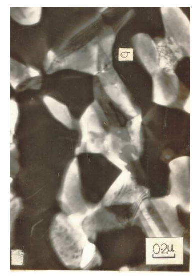
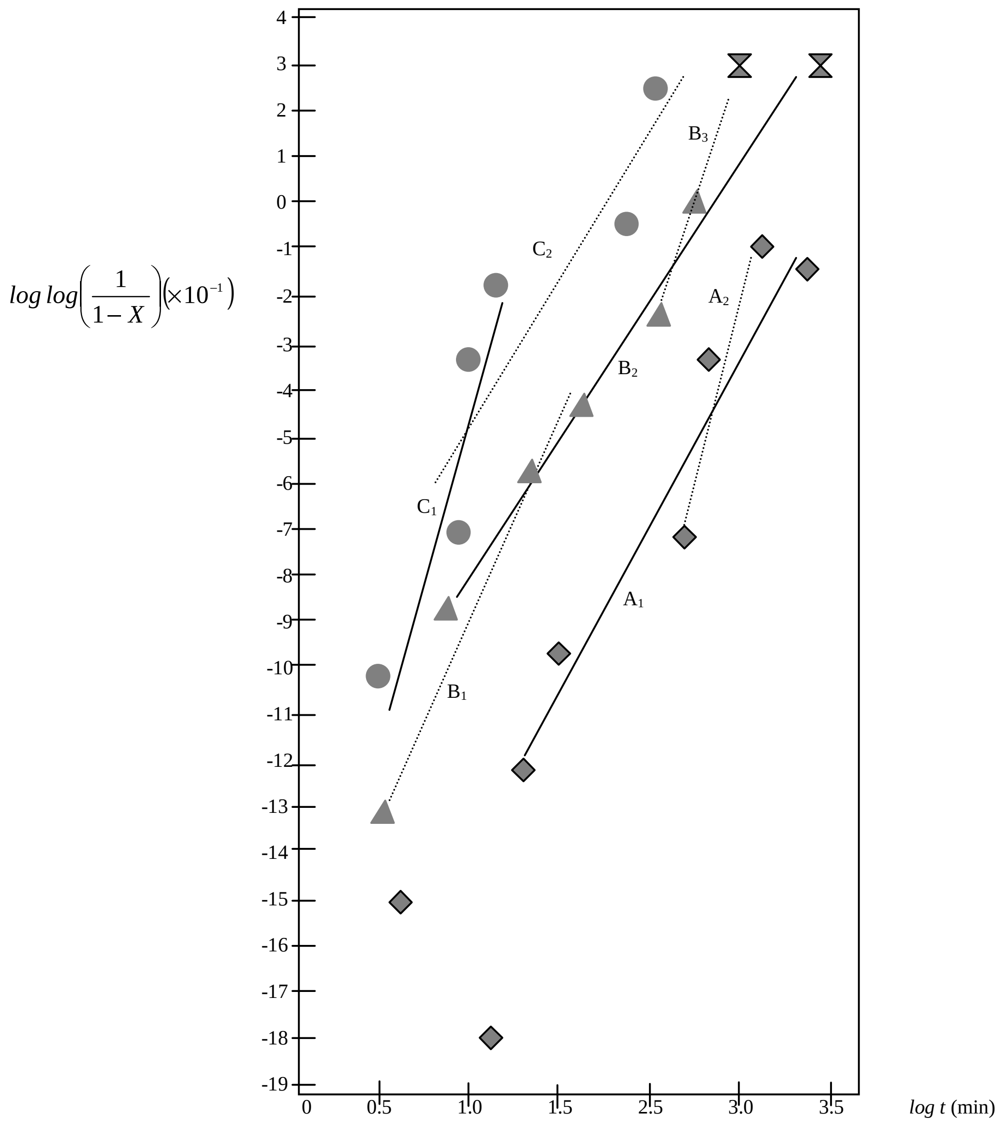


Plate 2: Bright field (BF) illustrates the occurrence of σ in the ferritic alloy. Alloy was deformed 80% at –196^{0}C and annealed at 700^{0}C.

Figure 1: Graph of $\log\log\left(\frac{1}{1-X}\right)$ *vs* $\log t$ for duplex and ferritic alloys deformed 20/80% at –1960C and annealed at 7000C up to 48 hours (X = fraction of ferrite transformed)



[18]. The different would be due to deformation of the samples (as done in the present work) prior to annealing.

Although the σ precipitation is sluggish the occurrence of γ_2 has considerable effect on it.

Deformation introduces dislocations and the associated stored energy provides driving force for the γ_2 precipitations which is of nucleation and growth mechanism, obeying the following law:

$$\dot{N} = A\exp\left(-\frac{Q}{RT}\right) \qquad (3.3)$$

where $\dot{N}$ = nucleation rate

A = constant

Q = activation energy

R and T = gas constant and absolute temperature

This deformation-induced greater rate of γ_2 precipitations implies greater nucleation sites (α/γ_2 boundary) for σ. Deformation of α would also result in recovery in the α-matrix leading to increased α/α boundaries. It is to be noted that σ precipitation initiates at α/γ_2 as well as α/α boundaries. Further, γ_2 precipitation would result in Cr-enrichment of the α and this favours σ precipitation. That deformation promotes the σ reaction is consistent with the k-values being greater for 80% reduction than the 20% reduction condition of the ferritic alloy. In fact the 20% reduction condition of the ferritic alloy has greater k-value than the same condition of the duplex. This is because, for the same condition of over-all reduction the α-phase in the duplex would be less deformed, as straining would be largely confined to the softer γ-phase.

4.0 Conclusion

Deformation has been found to increase the rate of sigma phase precipitation in the stainless steels. Deformation results in greater rate of $\alpha \rightarrow \gamma_2$ reaction and recovery of the α during subsequent annealing thus creating more sites (α/γ_2 and α/α boundaries) for σ precipitation. γ_2 occurrence, promoted by deformation is also associated with Cr enrichment of the α, and this also favours σ precipitation.

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