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Effects of martensite formation and austenite reversion on grain refining of AISI 304 stainless steel

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The austenite–martensite transformation followed by annealing for austenite reversion in AISI 304 stainless steel has been investigated in order to study the effect of this thermo-mechanical process on grain refinement. In particular the effect of cold reduction, annealing temperature and annealing times have been analysed. After getting ultrafine grains the effect of the grain size on the hardness and on the tensile properties has been evaluated, showing a Petch-Hall dependency in the fully analysed range (down to 0.8 μm grain size).

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1. Introduction

It is well known that the transformation of austenite to martensite is the basic reaction in the hardening of carbon steels [1]. It is less well known, however, that this transformation may also play an important role in austenitic stainless steels. According to Cohen *et al.* [2] the martensitic transformation is a nucleation-and-shear process with strain embryos as starting points for the transformation. For the martensite transformation, as for any other reaction, the following two conditions must be fulfilled:

- The free energy of the system must decrease during the transformation.
- Nuclei must be present.

Cohen suggested that screw dislocations constitute nuclei for martensite formation [2]. This was later proved by Krisement [3] in a theoretical study on martensite transformation. As a result of the large number of dislocations that exist even in a well annealed austenitic structure, more embryos are generally present than are necessary for the reaction to occur. The controlling factor for the kinetics of the transformation, therefore, is not the rate of nucleation, but the supply of free energy. The free energy change of the system must be large enough to enable the reaction to mount the activation barrier between the austenitic and martensitic states. Because martensite does not form spontaneously at the thermodynamic equilibrium temperature, an undercooling of about 200°C–300°C is usually required. Angel investigated this transformation in austenitic stainless steels and found that the amount of martensite increased with the degree of cold working and decreased with increasing working temperature [4].

Austenitic stainless steels have good corrosion resistance and good formability but they also have a relatively low yield strength. It is well known that the mechanical properties of austenitic stainless steels are very sensitive to the chemical composition (which can induce hardening by both substitutional and interstitial solid solution) and to grain size [5]. Recently developments have been carried out in stainless steels taking advantage of changes in the chemical composition induced by nitrogen addition [6].

Another effective way to increase yield strength without impairing ductility is grain refining. Since austenitic stainless steels do not undergo phase transformation at typical annealing temperatures, the only way to refine the grain is either by dynamic recrystallization imposing very severe deformations (uniaxial or multiaxial) [7] or by thermo-mechanical processes including both deformation and phase transformation [8].

Previous work has been carried out in order to study the effect of the dynamic recrystallization on the microstructure of AISI 304 stainless steel [9]. The present investigation has been carried out to analyse the effect of martensitic transformation and of the subsequent austenitic reversion on grain refining in an AISI 304 stainless steel.

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TABLE I Chemical composition of the material (mass%)

	C	Mn	Ni	Cr	Mo	N	Si
AISI 304	0.06	0.33	8.6	18.4	0.06	0.024	0.02

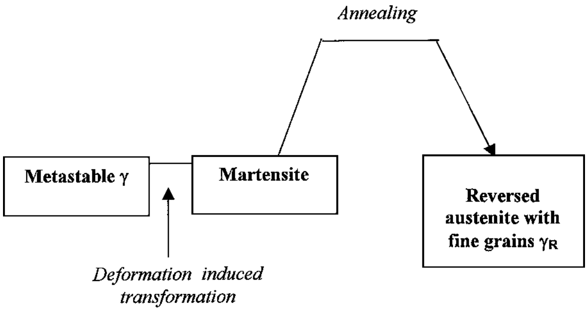


Figure 1 Thermo mechanical treatment adopted to obtain an ultra fine structure by reversion of martensite to austenite.

2. Materials and experimental details

The chemical composition of AISI 304 stainless steel, considered in this work, is shown in Table 1. Industrial hot rolled and annealed samples (50 × 200 mm), whose thickness were 3 mm, were cold rolled using different thickness reductions (from 5% to 90%). The grain size before cold reduction was approximatively 25 μm.

In order to analyse the effect of cold rolling temperature on martensite formation, the following procedure was carried out (Fig. 1). Cold reduction was carried out at two different temperatures: in the first case specimens were rolled after cooling in liquid nitrogen (about −100°C), in the latter they were deformed without any prior cooling (room temperature). In both cases the martensite content was measured after deformation by a ferritoscope. Deformation and martensite content were considered homogeneous within the samples. Quenched and cold rolled samples were then annealed at different temperatures (in the range 600°C–900°C), in order to investigate the martensite–austenite reversion. Samples were analysed after austenite reversion and automatic image analysis was used for the measure of grain size. Furthermore, in order to investigate the effect of grain size on the tensile properties of the steel, longitudinal ISO 50 tensile test specimens were cut from samples corresponding to different annealing conditions. Tensile tests were carried out with a deformation rate of 3 mm/min.

3. Results and discussion

3.1. Deformation

The curves of the martensite content M versus the true strain ε, are shown in Fig. 2 for cooled and deformed steel and for steel deformed with no prior cooling. In the cooled steel γ is almost completely transformed into martensite, while in the steel rolled without cooling, only 35% of martensite was produced after 90% cold reduction.

According to Angel [4] the expression found to fit these curves is:

$$M = \frac{k\varepsilon^n}{1 + k\varepsilon^n} \tag{1}$$

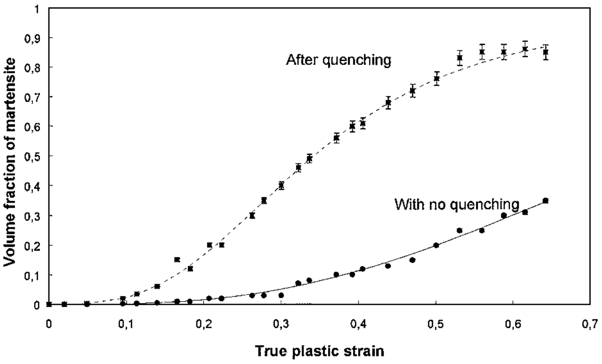


Figure 2 Formation of martensite by cold reduction with and without prior quenching in liquid nitrogen.

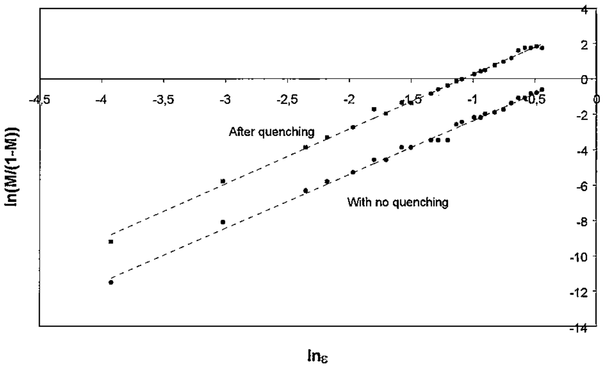


Figure 3 Log/log plot of the formation of martensite by cold reduction with and without prior quenching in liquid nitrogen.

where n and k are constants. Equation 1 is a log-auto-catalytic type given by Austin and Ricket [10] for the isothermal transformation of austenite, with strain instead of time. When the curves are plotted in a log/log scale, two parallel straight lines are obtained (Fig. 3). The slope n is equal to 3 in both cases and it is therefore temperature independent. The constant k, however, varies with temperature: in particular the higher the temperature, the lower the k value.

The slope of the curves shown in Fig. 2, i.e., the rate of reaction dM/dε, is zero at the beginning, gradually increasing to a maximum after a considerable amount of strain, and finally decreasing until no further transformation occurs with further straining, and a limiting value for the martensite content is reached.

The decreasing reaction rate per unit of austenite fraction can be regarded as depending both on a

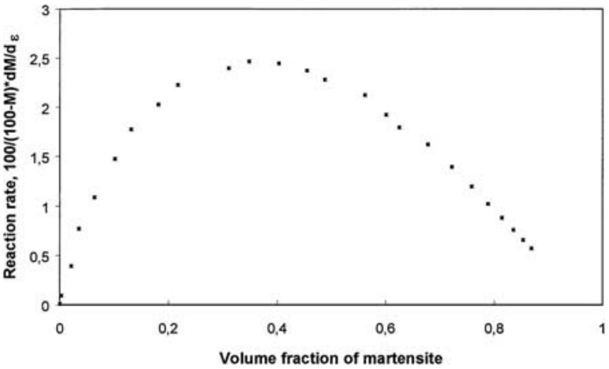
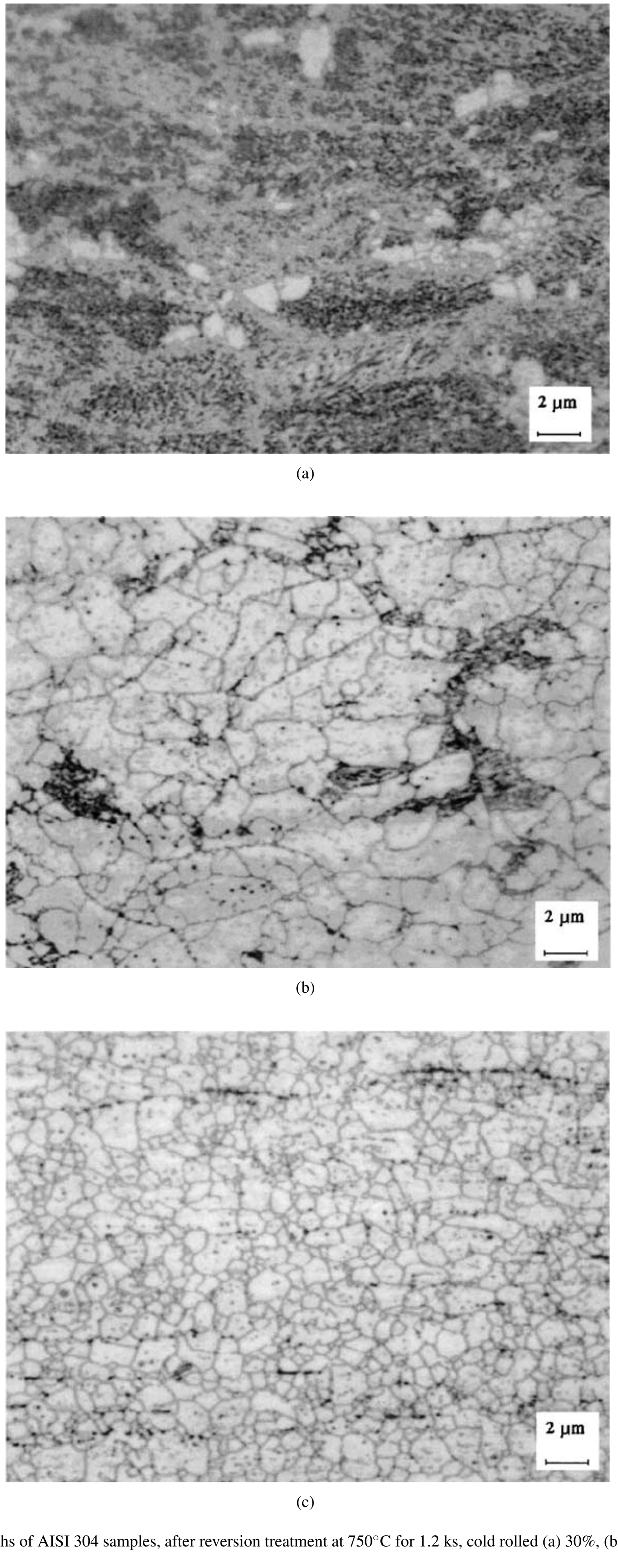


Figure 4 Rate of reaction per unit of austenite as a function of martensite content.



(a)

(b)

(c)

Figure 5 Optical micrographs of AISI 304 samples, after reversion treatment at 750°C for 1.2 ks, cold rolled (a) 30%, (b) 70%, (c) 90%.

stabilizing effect of deformation on the austenite, and on the decreasing amount of austenite available for transformation [4]. Accordingly, the rate of reaction per unit of austenite fraction, $\frac{100}{100-\mathrm{M}} \cdot \frac{\mathrm{dM}}{\mathrm{d}\varepsilon}$, is plotted against the content of martensite M in Fig. 4. It is clear that the low dM/dε value during the last stage of deformation (see Fig. 2) acts as a stabilizing effect on the reaction rate per unit of austenite fraction; on the contrary, the increasing dM/dε values during the first stages act as a catalyzing effect for the martensite transformation.

This data is in agreement with those from similar measurements performed by Takaki [11] who investigated the effect of cold working on the microstructure of deformation-induced martensite in austenitic stainless steels and found that in these materials the strain energy is mainly consumed by deformation-induced transformation of austenite up to 60% cold reduction, and for martensite deformation at higher reductions.

3.2. Microstructure after reversion treatment

3.2.1. Effect of cold rolling

Figs 5a, b and c show the microstructures of deformed samples of 30%, 70% and 90% respectively after reversion at 750°C for 1.2 ks. In the 30% deformed sample some austenitic grains begin to nucleate in the martensitic microstructure; in the 70% deformed sample, martensite has been almost completely consumed by the formation of new austenitic grains, but an inhomogeneous structure is evident (with a variation coefficient of grain size distribution $k = \frac{\sigma}{\bar{R}} = 0.58$ where σ and $\bar{R}$ are the standard deviation and mean grain size respectively); finally, when cold rolled reduction is increased up to 90%, the microstructure is fully recrystallised, the grain size distribution is more homogeneous ($k = \frac{\sigma}{\bar{R}} = 0.36$) and the average grain size is about 0.8 μm.

3.2.2. Time-temperature effect

In order to obtain homogeneous austenitic microstructures, 90% deformed samples were annealed at different temperatures (600°C–900°C) and times (10 s–1000 s).

Fig. 6 shows the evolution of martensite volume fraction in the 90% deformed sample as a function of annealing time and annealing temperatures. It can be observed that, as expected, the reversion rate increases with the annealing temperature. Fig. 6 can be used to determine the martensite-austenite reversion kinetics for this material. For instance, in the case of annealing at 600°C, 15% martensite is still present after 7 days; furthermore, at this temperature, for periods longer than 60 min the reversion process tends to be asymptotic, so that a complete reversion is possible only for very long times.

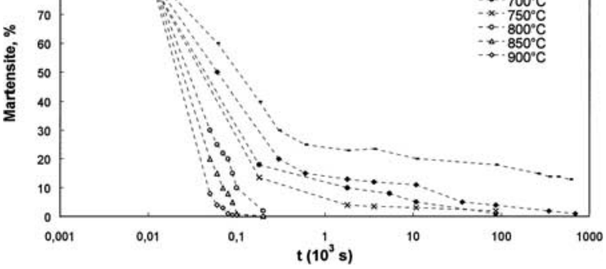
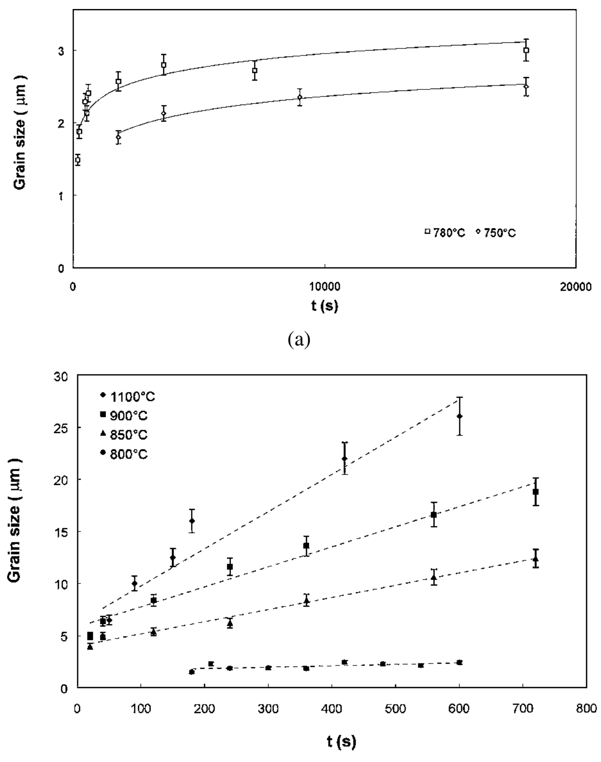


Figure 6 Effect of annealing time and temperature on the reversion behaviour of martensite induced by cold deformation.



(b)

Figure 7 Effect of annealing temperatures and times on the grain size.

The effect of annealing temperatures and times on the grain size is shown in Figs 7a and b. From these figures it is clear that for temperatures lower than 800°C, grain growth after recrystallisation is not activated while, for higher temperatures, thermally activated grain growth occurs, with a subsequent temperature upper limit to grain refining.

3.3. Grain size effect on the mechanical properties

Grain refining is commonly known to increase the hardness and the strength of grained materials. It is well known that the yield stress R_{p02} and the hardness HV of a metallic material increase with decreasing grain size d. In particular, the empirical Hall-Petch equation has been found to express the grain-size dependence of strength and hardness [12, 13]. In terms of strength and hardness, the Hall-Petch equations are $R_{\mathrm{p02}} = R^{0}_{\mathrm{p02}} + \mathrm{k}d^{-1/2}$ and $H = H_0 + \mathrm{k}'d^{-1/2}$, respectively, where the superscript 0 relates to the material of infinite grain size; k and k′ are constants representing the grain boundary as an obstacle to the propagation of deformation [1]. Fig. 8 shows the effects of the grain size on the stress-strain curves: it is clear that, the lower the grain size, the higher the yield strength and the lower the ductility of the steel. Fig. 9 shows the dependency

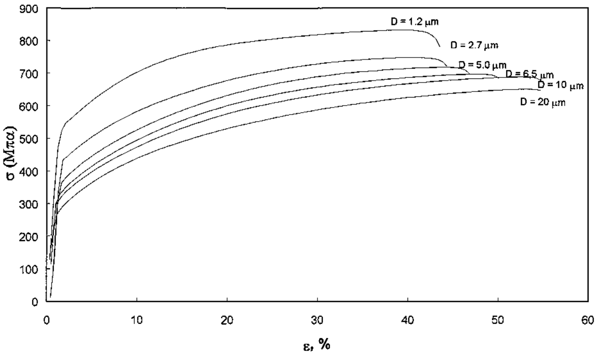


Figure 8 Effect of the grain size on the stress-strain curves.

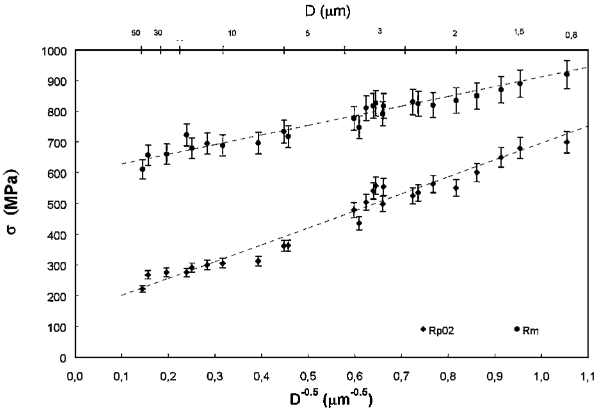


Figure 9 Dependency of yield strength and tensile strength on the grain size.

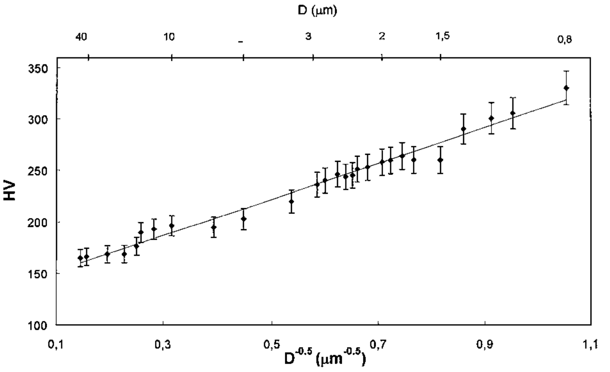


Figure 10 Dependency of the hardness on grain size.

of the yield stress (R_{p02}) and tensile strength (R_m) on grain size: it shows that both R_{p02} and R_m linearly increase with increasing $d^{-1/2}$. The same trend is shown in Fig. 10, where hardness versus grain size is shown. It means that, in the AISI 304 stainless steel, Hall-Petch relationships hold down to at least 0.8 μm of grain size. This result does not agree with that of similar measurements on AISI 301 stainless steel, where a deviation from the Hall-Petch relation was detected at about 3 μm grain size [14].

4. Conclusions

The deformation induced martensite transformation has been analysed in an AISI 304 stainless steel. The evolution of microstructure after austenite reversion at different annealing temperatures and times has been investigated. In particular, an ultrafine grain microstructure has been detected in low temperature annealed samples. The effect of grain size on the hardness and on the tensile properties of the steel has been analysed showing a Petch-Hall dependency in the fully analysed range (down to 0.8 μm grain size).

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