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To cite this article: T W Mukarati *et al* 2018 *IOP Conf. Ser.: Mater. Sci. Eng.* **430** 012042

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The direct observation of surface martensite formation upon cooling to temperatures close to ambient in a heat treated AISI 301 stainless steel

T W Mukarati^{1,*}, R J Mostert¹ and C W Siyasiya¹

¹ University of Pretoria, Private bag X20 Hatfield 0028, South Africa

^a tmcarati@gmail.com

Abstract. Martensitic transformation, either athermal or strain-induced, in metastable AISI 301 austenitic steel is of high technical interest as this facilitates manipulation of mechanical properties. This work is part of a project aimed at identifying the influence of variables that determine the athermal α' -martensitic transformation in this steel in order to ensure consistent martensite formation and optimized mechanical properties. The influences of initial austenitic grain size and surface concentrations of interstitial elements (C, N) on martensite start temperature were investigated. The surface concentrations of both carbon and nitrogen were decreased through decarburisation and the formation of martensite upon cooling from ambient temperatures was directly observed using a cryogenic Scanning Electron Microscope (cryo-SEM). It was found that martensite formed on the heat-treated surfaces at much higher temperatures than that expected for AISI 301 steel. The observations were confirmed using electron backscatter diffraction (EBSD). Other analytical techniques including glow-discharge optical emission spectroscopy (GDOES), and Neutron Diffraction were carried out to explain the observations.

1. Introduction

The AISI 301 austenitic stainless steel is lean in alloying elements and hence leads to a greater susceptibility to formation of strain-induced martensite (SIM) upon cold deformation. The metastable austenitic microstructure can transform to martensite through either cold deformation or thermal cooling [1], [2]. Martensitic transformation, is of great interest and crucial as mechanical properties can be boosted greatly with this phase transformation [3].

Understanding microstructural evolution is the key in developing a comprehensive constitutive model for material behaviour [4] for this steel type. The optimization of the microstructure is needed to control the mechanical properties [5] and to ensure cast-to-cast consistency of such properties.

Carbon and nitrogen are two interstitial elements which are known to thermodynamically stabilize the austenite phase and also suppress strain-induced martensitic transformation upon cold deformation [5]. Figure 1 shows that nitrogen has a stronger austenite stabilization effect compared to carbon and an addition of 0.1% (mass) nitrogen, results in the decrease of M_s temperature by more than 300 Kelvin for an austenitic stainless steel.



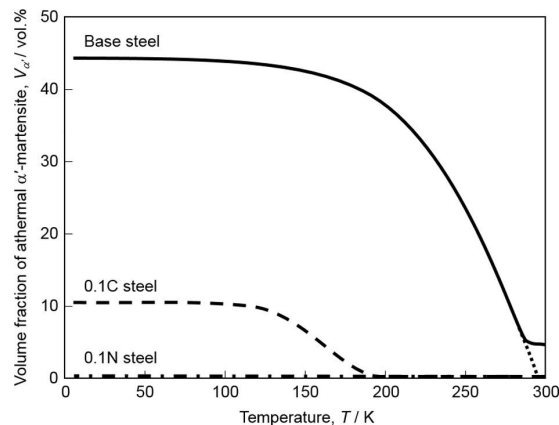


Figure 1. Changes in volume fraction of athermal α' -martensite upon cryogenic cooling [5] for a Fe- 18% Cr- 8% Ni base steel showing the influence of additions of carbon and nitrogen.

2. Materials and methods

The starting materials were hot rolled, annealed and pickled AISI 301 stainless steel plates of 4.44 mm thickness. As-received samples were cut into three samples of 300mm x 30mm. Two samples were heat treated at 1448 K and 1648 K in air for 10.5 minutes and were both air cooled. The three samples (15 mm x 15 mm surface area): as-received, heat treated at 1448 K and 1648 K were electropolished and characterized in the unetched condition using cryogenic SEM (Zeiss Crossbeam 540 FEG SEM), which is equipped with cooling facility using liquid nitrogen. In order to observe microstructural changes, the same spot of the sample surface was analyzed using the in-lens detector of the microscope as the temperature was lowered. The samples were thereafter analyzed using optical microscopy and electron back scattered diffraction.

Analysis such as GDOES was done on the plant and laboratory annealed samples to determine the change in surface concentration of interstitial elements (C, N). Interrupted cryogenic neutron diffraction analysis was done on the as-received sample with 15 analysis temperatures used between ambient and 3 K. EBSD analysis was carried out using EBSD Oxford instrument at an accelerating voltage of 20kV and a working distance of 10 mm. The samples for cryogenic SEM and EBSD were prepared by electropolishing using a Struers Lectropol-5 equipment and A3 electrolyte (600 ml methanol + 360 ml butoxyethanol + 60 ml perchloric acid) and operating voltage of 35 V at room temperature. No etching was done.

3. Results and discussion

The chemical composition (in wt. %) of the as-received hot rolled, annealed and pickled AISI 301 coil is given in Table 1.

The equilibrium thermodynamic stability of the phases of this steel was calculated as a function of temperature ranging from 1220 K to 1740 K, using Thermo-Calc software, as shown in Figure 2. Figure 3 and Table 2 demonstrate the strong effect of the annealing temperature on austenite grain size, with an increase from 1353 K (Fig 3a) to 1448K (Fig. 3. B) resulting in more than doubling the grain size. Figure 4 relays the Neutron diffraction spectra before and after cooling the as-received sample to 4 K in a cryogenic neutron diffraction facility, showing no observed crystallographic changes due to the cooling. The interrupted in-situ neutron diffraction results observed between 300 K 3 K did not identify any transformation of the austenite of the as-received sample. Figure 5 and 6 present SEM images obtained during in-situ observation of the as-polished surface with cryogenic cooling of the 1448 K laboratory annealed sample. Accordingly, a small quantity of martensite could be observed at room temperature, but the martensite fraction increased significantly upon cooling to 243 K (b) and 125 K (c). Figure 6 present SEM images taken at high magnification (5000 times) showing very thin

parallel lines (ϵ -martensite) which acts as an intermediate phase for formation of α' -martensite. These in-situ observations of martensite formation at relatively low degrees of undercooling were obviously surprising and in contrast with the neutron diffraction and previously published, [5], (Fig. 1, for example) results. Similar results were observed for the 1648 K laboratory annealed sample. The GDOES analyses of the plant and laboratory annealed (in air) surface chemistry, as far as the interstitial element concentrations are concerned, are given in table 2. Accordingly, it is clear that the laboratory heat treatments in air resulted in removal of most of the surface carbon and a substantial portion of the surface nitrogen [6], [7]. In order to confirm the direct observation of martensite formation in the cryogenic SEM, the samples were thereafter analysed using EBSD and optical microscope at room temperature, as shown in Figure 7 and 8.

Table 1. Chemical composition (spectrographic analysis) of annealed and pickled AISI 301 as supplied (mass %).

C	Mn	P	S	Si	Cr	Ni	N ₂	Co
0.02	1.57	0.023	0.003	0.41	17.41	6.6	0.119	0.12
Cu	Mo	Sn	Ti	Al	Nb	O	B	Fe
0.09	0.05	0.009	0.009	0.005	0.009	0.0074	0.0017	Balance

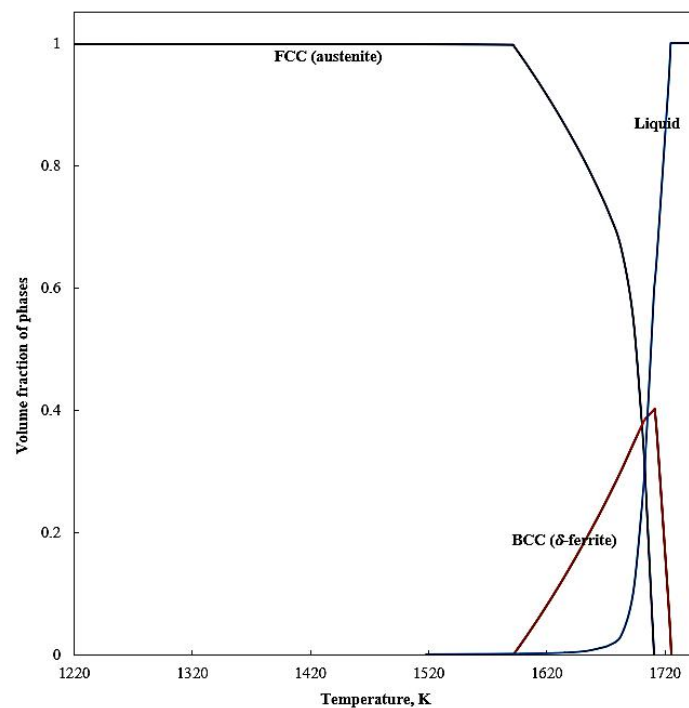


Figure 2. Thermo-Calc for the given chemistry in Table 1.

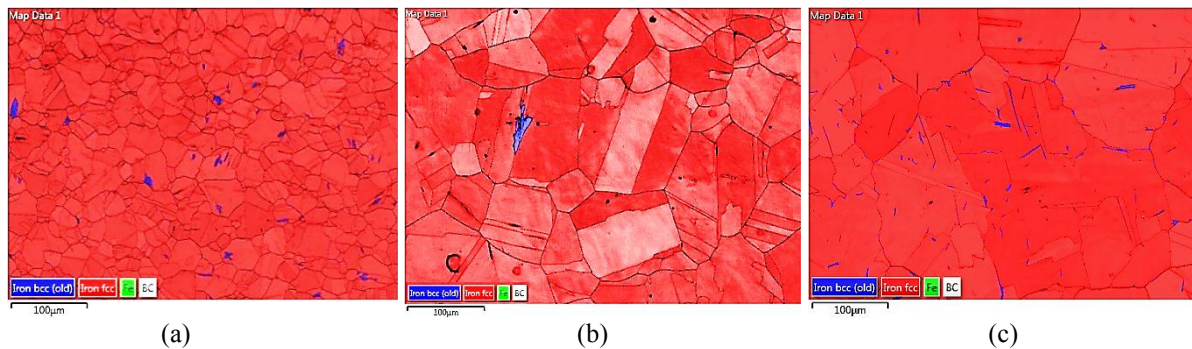


Figure 3. EBSD images of (a) as-received hot rolled, annealed and pickled AISI 301 stainless steel (b) heat treated at 1448K and (c) heat treated at 1648K, all taken before cryogenic work.

Table 2. The surface chemical composition of carbon and nitrogen of the as-received and laboratory annealed samples, as obtained using GDOES.

	As received (plant annealed at 1353K)	Annealed at 1448 K	Annealed at 1648 K
Carbon (%wt)	0.0174	0.0030	0.0038
N ₂ (%wt)	0.1190	0.0574	0.0603
*Initial austenitic grain size (µm).	25.0	59.5	102.7

*The initial austenitic grain sizes were determined using Tango software of the EBSD.

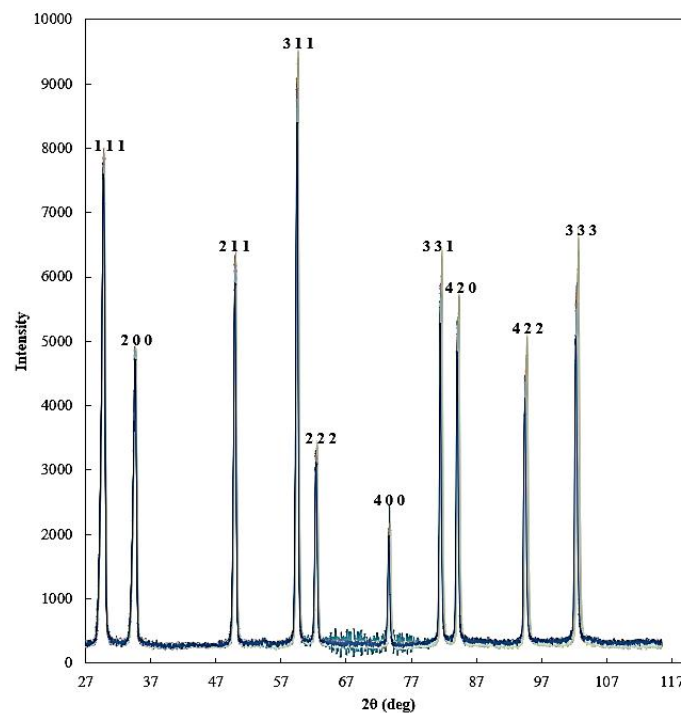


Figure 4. Neutron diffraction analysis of steel in ‘as-received’ condition at 300 K, 250 K, 245 K, 242 K, 238 K, 235 K, 233 K, 230 K, 227 K, 224 K, 220 K, 200 K, 150 K, 100 K, and 3 K, with the spectra unchanged throughout the temperature range.

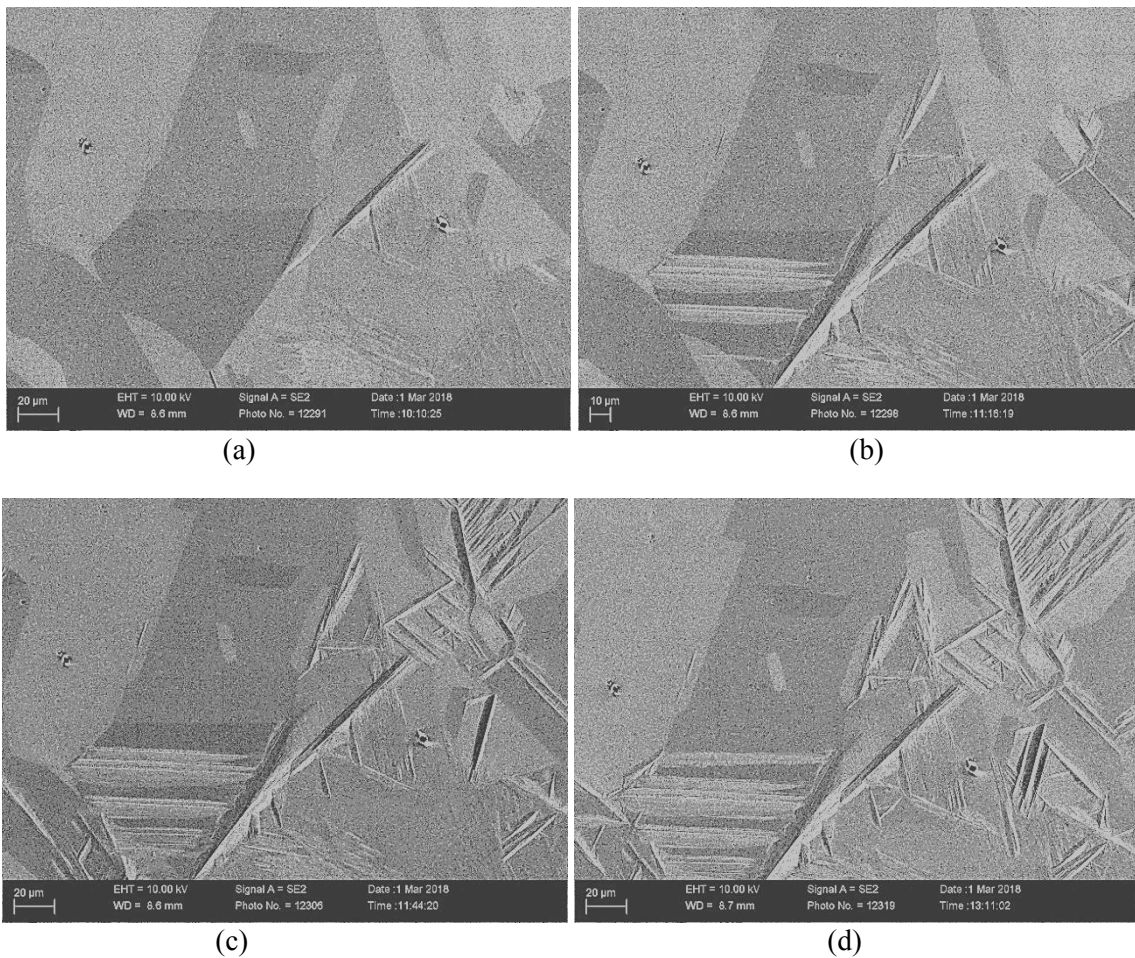


Figure 5. Images of microstructures from the cryogenic SEM at the same location showing formation of α' -martensite of the affected surface on cryogenic cooling (steel annealed at 1448 K after) (a) at room temperature, (b) 243 K, (c) 233 K (d) 125 K, all taken at 1000 mag.

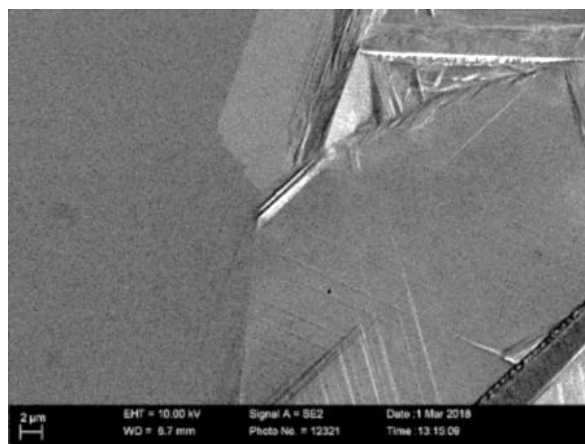


Figure 6. Microstructure showing thin parallel lines, (ϵ -martensite) which acts as an intermediate phase for formation of α' -martensite at 125 K at high magnification.

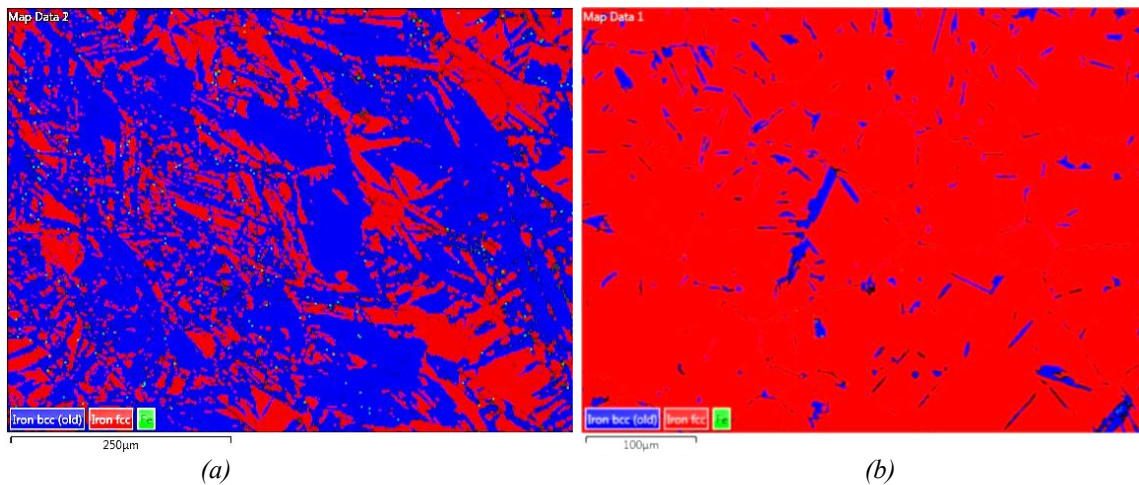


Figure 7. EBSD images of steel annealed at (a) 1448 K, (b) 1648 K after cryogenic cooling to 123 K.

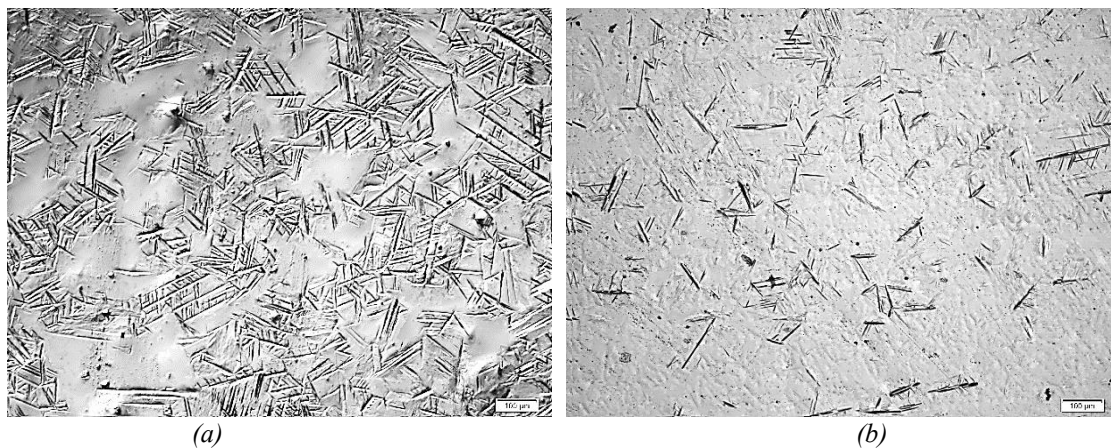


Figure 8. Optical images of steel annealed at (a) 1448 K, (b) 1648K after cryogenic cooling to 123 K.

The ‘as-received’ steel had been plant annealed at 1353 K in a continuous annealing furnace. For this base steel, no α' -martensite transformation was observed during cryogenic cooling and neutron diffraction analysis cooling the sample down to a temperature as low as 4 Kelvin. Samples which were laboratory annealed at 1448 K and 1648 K have however shown α' -martensite developing at relatively elevated temperatures during cryogenic cooling using a cryogenic SEM. Specific spots of the electropolished samples were selected using the in-lens detector of Zeiss Crossbeam 540 FEG SEM whilst the temperature was lowered by liquid nitrogen. Coarse α' -martensite were observed to form at temperatures of 243 K and lower. At high magnification, very thin parallel lines were observed. This was believed to be ϵ -martensite which acts as an intermediate phase for the $\gamma \rightarrow \alpha'$ transformation. According to the published results, M_s for this steel [5] in the as-received condition cannot be observed above zero Kelvin. The direct observation of martensite development on the electropolished surfaces at much higher temperatures after heat treatment in air at 1448 K and 1648 K, is believed to be due to localised decarburization and denitriding during laboratory annealing in air, as demonstrated by the GDOES analyses performed. The calculated M_s temperature for the surface chemistries of the laboratory annealed (1448K and 1648K annealed samples) were found to be much higher than that of the bulk composition; 184.5 K and 173.5 K respectively for the two annealing temperatures using the Eichelman and Hull equation [8]. The observed M_s temperatures of the laboratory annealed surfaces were in the order of 243 K and 228 K respectively, and it is believed that the deviation of actual from calculated M_s temperatures are probably due to grain size effects with larger grain sizes leading to higher M_s -temperatures. Martensitic transformations are autocatalytic as martensite laths partition the

grain on reaching the grain boundaries thereby inducing the formation of other laths. Martensitic transformation of decarburized and denitrified surfaces in industrial plants can therefore accelerate bulk martensitic transformation during subsequent straining and lead to variable mechanical properties in metastable stainless steels.

The Thermo-Calc model demonstrated that, for the bulk composition, formation of δ -ferrite occurs from around 1573 K. EBSD images of the steel annealed at 1648 K showed a significant percentage of δ -ferrite, approximately 11.4% (volume fraction of 0.11). Formation of δ -ferrite (bcc) from austenite (fcc) implies a significant amount of interstitial elements such as nitrogen and carbon released into the solution which will then stabilize austenite further. This effect was observed by a smaller volume fraction of α' -martensite forming during cryogenic cooling as compared to the steel annealed at 1448 K where there was no formation of δ -ferrite.

4. Conclusions

For the metastable AISI 301 stainless steel investigated, the formation of α' -martensite on the surface is possible at temperatures close to ambient, due to decarburization and denitriding of the surface. In a production environment, this unexpected martensitic transformation could cause variable responses to strain hardening due to the autocatalytic nature of the austenite to martensite transformation. An inert gas atmosphere is therefore recommended during plant annealing to prevent changes in surface chemistry through decarburization and denitriding.

Acknowledgements

The authors are grateful to Columbus Stainless Steel company for financial support as well as the material, AMI-FMDN, administered by Mintek for supporting this work, Laboratory for Microscopy and Microanalysis (University of Pretoria) and NECSA (South Africa) for their service and assistance.

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