

An *In Situ* High-Temperature X-Ray Diffraction Study of Phase Transformations in Maraging 300 Steel

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Abstract. An *in situ* high-temperature X-ray diffraction (HTXRD) study in maraging 300 steel was carried out to study the martensite to austenite transformation and effect of time of exposure in the austenite reversion below austenite start temperature. Solution annealed materials were subjected to controlled heating-holding cycles. The first sample was heated at a rate of 10 °C/min from room temperature to 800 °C, showing that the microstructure is completely martensitic (α'_{110}) until 600 °C. From 650 °C until 800 °C, the microstructure is gradually changing from martensitic to austenitic, showed by the increasing peaks of γ_{111} and reducing peaks of α'_{110} . At 800 °C the microstructure is completely austenitic (γ_{111}). Another sample was heated at 10 °C/min from room temperature to 600 °C and held for 4 hours. At 600 °C, at 0 h time of exposure, only a martensitic peak was observed. An austenite peak can be observed after some time of exposure at this temperature. The volume fraction of austenite increased with increasing time of exposure at 600 °C, reaching 50/50 volume fraction after 4 hours of exposure. XRD diffraction patterns for the same sample that was held for 4 hours at 600 °C and then cooled down in air to room temperature showed the same intensity of austenite and martensitic peaks found *in situ* at 600 °C for 4 hours (retained austenite), with the volume fraction of 50/50 of austenite and martensite phases. The HTXRD technique can be used to identify and quantify martensite to austenite transformation and austenite retention.

Introduction

Maraging steels are well known for their outstanding combination of strength, fracture toughness and machinability in the solution-annealed condition with minimum distortion during subsequent aging. After solution annealing at the usual temperature of 820 °C for 1 hour results in a microstructure which is predominantly soft–martensite, which is then hardened by the precipitation of intermetallic compounds by aging at the usual temperature of 480 °C for 3 hours. Consequently, maraging steels have many applications, for example in the manufacture of crankshafts, gears, tools, rocket and missile casings. Maraging 300 steel is a member of the 18% nickel-based alloy family [1-4].

With long aging times and/or high temperature, even below the A_s (austenite start), the structure tends to revert to the equilibrium phases - primarily ferrite and austenite, since it is a diffusion-controlled process. Dissolution of metastable nickel-rich precipitate particles in favor of equilibrium iron-rich precipitates locally enriches the matrix in nickel, which favors austenite formation. Very substantial amounts of austenite (of the order of 50%) can eventually be formed by overaging. Austenite is a stable phase at room temperature for maraging steel compositions. The presence of retained austenite is generally considered unacceptable because this phase can result in significant variations in tensile strength, ductility, and toughness [1-7]. There have been many attempts to study the phase transformation behavior of maraging steels, mainly by dilatometry [8-10]. There has been no attempt made to explain the phase transformation behavior of maraging steels with the help of high-temperature X-ray diffraction (HTXRD) technique. In this work, the HTXRD technique was used to study the phase transformation and martensite reversion to austenite, even below A_s , of maraging 300 steel.

Experimental Procedure

The material investigated in this study is a maraging 300 steel solution annealed at 820 °C for 1 h and then air-cooled. Table 1 shows the chemical composition of the steel.

Table 1 – Chemical composition [wt.%] of the maraging 300

| Co | Mo | Ni | Ti | Al | C | S | P | Si | Mn | Fe |
|------|------|-------|------|------|-------|-------|-------|------|------|---------|
| 9.37 | 4.94 | 19.00 | 0.63 | 0.08 | 0.008 | 0.002 | 0.004 | 0.06 | 0.01 | Balance |

The samples were prepared as parallelepiped pieces of 20 mm length, 6 mm width and 1 mm thickness. The in situ high-temperature X-ray diffraction (HTXRD) and room temperature X-ray diffraction (XRD) were carried out by using a Rigaku model Ultima IV diffractometer with a $Cu\alpha$ radiation ($\lambda = 0.15405$ nm) from a rotating anode (at 45 kV/40mA), on which a high-temperature chamber was mounted. Two thermal cycles were studied. One of them comprised heating from room temperature to 800 °C at a heating rate of 10 °C/min. During heating ramps, the sample was held at different temperatures (400, 500, 600, 650, 700 and 800 °C) for XRD analysis and then the heating was continued. In the other cycle, the sample was heated from room temperature to 600 °C at heating rate of 10 °C/min. The sample was held at this temperature for XRD analysis after 0, 0.25, 1, 2, 3 and 4 hours, consecutively. Finally, the samples that were held at 600 °C for 4 hours was cooled down to room temperature for XRD analysis.

Results and Discussion

Figure 1 shows the sequence of X-ray diffraction patterns in the 2θ range 42–46° recorded during heating of a sample with a heating rate of 10 °C/min from room temperature to 800 °C, showing the more representative peaks of the martensite α'_{110} and austenite γ_{111} .

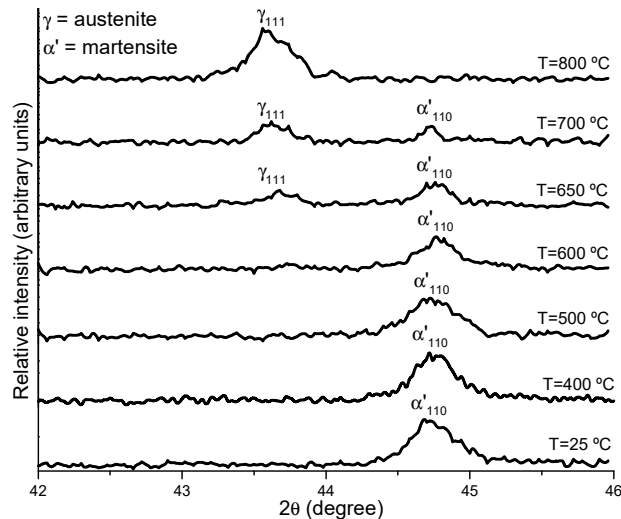


Fig. 1 – Sequence of X-ray diffraction patterns recorded upon heating rate of 10 °C/min from room temperature to 800 °C showing peaks corresponding to the martensite and austenite phases.

According to Fig. 1, from room temperature until 600 °C the microstructure of the solution annealed is completely martensitic (α'_{110}). From 650 °C until 800 °C, the microstructure is gradually changing from martensitic to austenitic, showed by the increasing peak of γ_{111} and reducing peak of α'_{110} . At 800 °C the microstructure is completely austenitic (γ_{111}). These results are according to the results reported in the literature of maraging 300 dilatometry [8-10]. Reis et al [10] reported with the same maraging 300 steel an A_s (Austenite formation start) of 623 °C and A_f (Austenite formation finish) of 801 °C.

Fig. 2 displays the sequence of HTXRD spectra in the 2θ range 42–46° during heating of other sample at 10 °C/min from room temperature to 600 °C and held for 4 hours. Fig. 3 shows the volume fraction of martensite and reverted austenite phases versus time of exposure calculated from the sequence of X-ray diffraction patterns from Fig. 2. The volume fraction of austenite can be estimated from the α'_{110} and γ_{111} peaks of martensite and austenite, respectively, as per the direct comparison method [11].

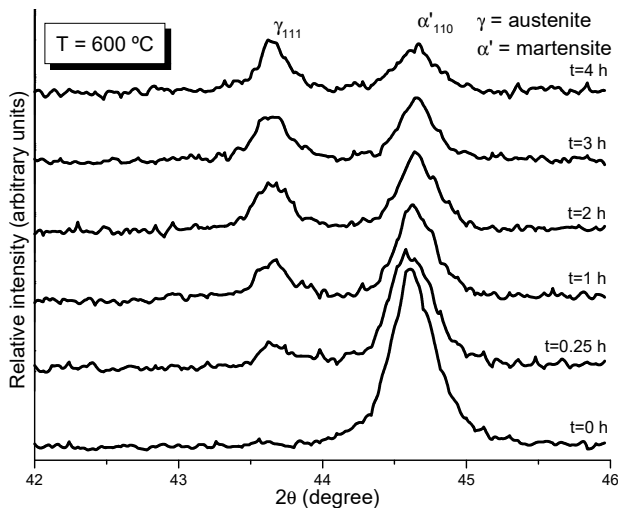


Fig. 2 – Sequence of X-ray diffraction patterns recorded upon heating rate of 10 °C/min from room temperature and held at 600 °C for 4 hours showing peaks corresponding to the martensite and austenite phases.

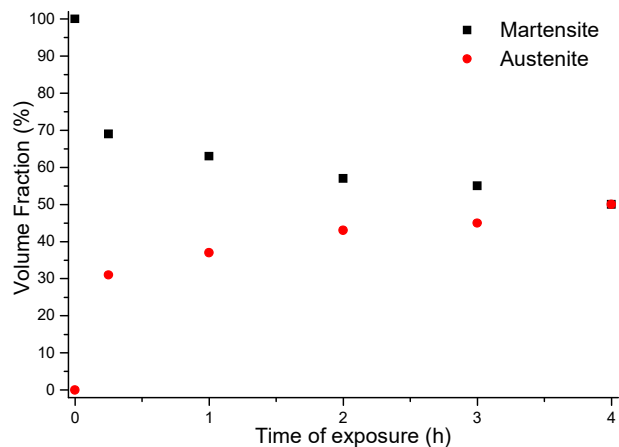


Fig. 3 – Volume fraction of martensite and reverted austenite phases versus time of exposure calculated from sequence of X-ray diffraction patterns from Fig. 2.

It is observed from Fig. 2 and Fig. 3 the influence of high temperature (600 °C) exposure time in the martensite reversion to austenite. At 600 °C it is expected to observe only the martensitic peak (α'_{110}), since it is below the A_s , and this is the result initially. Otherwise, the austenite peak

(γ_{111}) can be observed after some time of exposure at this temperature. The volume fraction of austenite increased with increasing time of exposure at 600 °C, reaching 50/50 volume fraction of austenite and martensite after 4 hours of exposure. Austenite reversion in maraging steels can occur when these alloys are held at temperatures below the A_s for prolonged periods, because the martensite that is formed during solution treatment is metastable and the system decomposes to the equilibrium austenite and ferrite structures via diffusion-controlled reactions. Dissolution of metastable nickel-rich precipitate particles in favor of equilibrium iron-rich precipitates locally enriches the matrix in nickel, which favors austenite formation. In these nickel-enriched regions, the aging temperature of 600 °C is, therefore, higher than the transition temperature of martensite to austenite. Increasing the exposure time at 600 °C, more nickel-enriched is available in some areas of the matrix, and more martensite is converted to austenite. There is an equilibrium volume fraction of austenite as function of temperature [1-7].

The sample that was held for 4 hours at 600 °C was cooled down in air to room temperature. Fig.4 shows the X-ray diffraction pattern after the cooling.

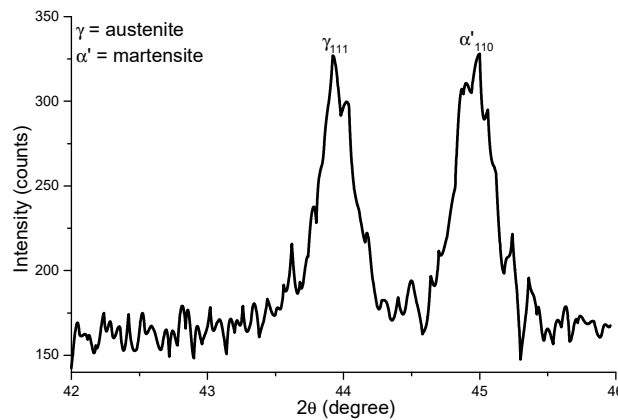


Fig. 4 – XRD diffraction patterns for the sample that was held for 4 hours at 600 °C and then cooled down in air to room temperature showing peaks corresponding to the martensite and austenite phases.

From Fig. 4 it can be noticed that the same intensity of austenite peak (γ_{111}) and martensitic peak (α'_{110}) found at 600 °C for 4 hours was found after the sample was cooled down to room temperature (retained austenite). The volume fraction is 50/50 of austenite and martensite phases. The reason is that the sample was overaged at 600 °C for 4 hours. Nickel-enriched regions actually stabilize the austenite at room temperature, as they are present in higher concentration, and the austenite is not converted to martensite [1-7].

Conclusion

The following conclusions were drawn based on the present work on maraging 300 steel:

- In situ high-temperature X-ray diffraction (HTXRD) can be used to identify martensite to austenite phase transformation of maraging 300 steel;
- Austenite reversion can be observed by HTXRD, even below A_s . Since it is a diffusion-controlled reaction, the time of exposure affects the volume fraction of reverted austenite;
- Austenite reverted at high temperature is retained at room temperature. The volume fractions of austenite and martensite found by HTXRD are similar at room temperature XRD after the sample is cooled.

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