

Magnetic determination of the thermal stability of retained austenite in TRIP steel

Lie Zhao, Ojiyed Tegus, Ekkes Brück, Niels H. van Dijk, Suzelotte O. Kruijver, Jilt Sietsma and Sybrand van der Zwaag

The martensitic transformation of retained austenite in a 0.20C-1.52Mn-0.25Si-0.96Al (mass contents in %) TRIP steel is investigated using thermo-magnetic measurements in the temperature range between 300 K and 5 K at a constant magnetic field of 5 T. In addition, the transformation is studied by X-ray diffraction and thermodynamic analysis. From the difference of magnetisation during heating and cooling processes the temperature dependent austenite fraction is determined, which fits well with the prediction from a thermodynamic model. It is also found that nearly all austenite transforms athermally to martensite upon cooling to 5 K and the transformation start and finish temperatures are 355 K and 114 K. The measured thermal stability is related to the carbon concentration of individual austenite grains.

Aims and scope

Low-alloy multiphase transformation-induced plasticity (TRIP) steels have attracted more and more interest in recent years due to their high strength and enhanced formability [1; 2]. Detailed insight in the stability range of retained austenite is regarded to be of the highest importance for controlling the materials properties. The mechanical stability of retained austenite as a function of imposed stress or strain is usually described by the Ludwigson and Berger relation [1...4] or is linked to the martensite starting temperature under stress, M_s^σ [5]. No work on the thermal stability of retained austenite in TRIP steels has been reported, although such studies can give useful information on the variation in the stability for individual retained austenite grains.

On the other hand, the martensitic transformation itself in engineering steels has been widely investigated. It is known that the amount of athermal martensite formed is only a function of temperature and independent of the holding time. In order to describe the increase in martensitic formation with increasing undercooling below the martensite start (M_s) temperature, many empirical or theoretical equations have been proposed which include a linear relationship, a power relationship and an exponential relationship [6]. In addition, Yu et al. [6; 7] developed a relationship based on the thermodynamic analysis of the martensitic transformation:

$$f^{\alpha'} = \frac{M_s - T}{M_s - \beta M_f - (1 - \beta)T}, \quad (1)$$

where $f^{\alpha'}$ is the fraction martensite, T is temperature, and β is the ratio of the slopes of the temperature dependence

of the Gibbs free energy for martensite (α') and austenite (γ). The predicted results from equation (1) were found to be consistent with the experimental results in high-carbon chromium-alloyed steel. The present work aims at measuring the athermal martensitic transformation of retained austenite in a TRIP steel, at analysing the transformation behaviour on the basis of such a thermodynamic analysis, and at relating the austenite stability to the carbon concentration.

Experimental procedures

A 0.20C-1.52Mn-0.25Si-0.96Al (mass contents in %) TRIP steel was produced via hot rolling and air cooling. The as-received material had a thickness of 6 mm. This material was machined to cylindrical samples with a diameter of 5 mm and a length of 10 mm which were then heat-treated in a Bähr 805a dilatometer. The samples were pre-annealed for 600 s at 1173 K, which is in the two-phase region, and then quenched to 673 K at 100 K/s, held at this temperature for 90 s, and subsequently quenched to room temperature. This heat treatment yields a multiphase microstructure (ferrite, bainite, martensite and retained austenite) with a maximum volume fraction of retained austenite and an absence of carbide precipitates [8].

For the magnetic measurements and X-ray diffraction (XRD) measurements, the heat-treated samples were cut along the direction perpendicular to the cylindrical axis into disks with a diameter of 5 mm and a thickness of about 1 mm. The cutting was performed using a travelling wire electronic discharging machine (EDM). Low force was applied during cutting in order to avoid a stress-induced transformation of the retained austenite. The magnetisation measurements were performed on a Quantum Design SQUID magnetometer (MPMS-5S). During the measurement, the sample was thermally cycled twice from 300 to 5 K at a constant magnetic field of 5 T. Heating and cooling rates were very low (about 0.5 K/min) so that it can be assumed that the sample is in the equilibrium condition. The applied magnetic field is sufficiently large to approach the magnetic saturation according to previous investigations [9].

In order to compare the results from the magnetic measurements, additional XRD measurements at room temperature were performed on a Bruker D5005 X-ray dif-

Dr. Lie Zhao, postdoctoral researcher; *Dr. Suzelotte O. Kruijver*, research assistant; *Dr. ir. Sybrand van der Zwaag*, professor, Steel Production Cluster, Netherlands Institute for Metals Research, also in Laboratory for Materials Science; *Dr. ir. Jilt Sietsma*, associate professor, Laboratory for Materials Science; *Dr. ir. Niels H. van Dijk*, scientist, Interfaculty Reactor Institute, Delft University of Technology, Delft; *MSc. Ojiyed Tegus*, research assistant; *Dr. Ekkes Brück*, scientist, Van der Waals – Zeeman Institute, University of Amsterdam, Amsterdam, The Netherlands.

fractometer using $\text{CoK}\alpha$ radiation for the as-received, the heat-treated and the thermally-cycled samples. From the XRD results, the volume fraction of retained austenite was calculated from the ratio between measured and theoretical intensities of the austenite and ferrite diffraction peaks [4; 8; 10]. The carbon concentration in the retained austenite is calculated from the lattice parameter using Cohen's method [11].

To analyse the chemical driving force for the martensitic transformation, the Gibbs free energy of austenite and martensite was calculated employing the computational thermodynamics program MTDData (version 4.71). The SGTE (Scientific Group Thermodata Europe) database was employed during the calculations.

Evaluation and discussion of the results

Temperature dependence of magnetisation. Figure 1 depicts the mass magnetisation as a function of temperature at a constant magnetic field of 5 T during the first thermal cycle from 300 to 5 K and back. The magnetisation increases significantly with decreasing temperature. This is due to the increase in the saturation of ferromagnetic phases, ferrite and martensite, and in case of cooling, an additional increase is due to the increase of martensite formed from retained austenite with decreasing temperature. The temperature dependent saturation magnetisation, $M(T)$, can be described by the following equation [12; 13]:

$$M(T) = M_0 \left(1 - AT^{3/2}\right) \cdot f \quad (2)$$

where A is a constant, M_0 is the saturation magnetisation at 0 K and f is the fraction of ferromagnetic phases. For pure iron, $A = 3.4 \cdot 10^{-6} \text{ K}^{-3/2}$ and $M_0 = 221.9 \text{ A}\cdot\text{m}^2/\text{kg}$ [12]. For the present steel, A and M_0 are determined to be $4.6 \cdot 10^{-6} \text{ K}^{-3/2}$ and $195 \text{ A}\cdot\text{m}^2/\text{kg}$, respectively, from the heating curve in which f is 1. The difference in M_0 between pure iron and the present steel can be mainly due to the fact that the addition of alloying elements in the steel and a lower saturation magnetisation for the martensite phase [14] lead to a decrease in M_0 . In addition, the specimen might be not completely saturated at the applied magnetic field of 5 T at low temperatures close to 5 K [14]. The cooling curve in figure 1 is dependent not only on the temperature but also on the fraction of ferromagnetic phases, which will be further analysed in the following section.

To confirm whether the austenite has been completely transformed, a second thermal cycle at a constant magnetic field of 5 T was run. The results from the second cycle show that both cooling and heating curves nearly coincide with the heating curve during the first cycle, indicating that no further transformation occurred during the second thermal cycle. Furthermore, to examine the effect of the isothermal holding time on the kinetics of martensitic transformation, as observed in high alloy steels and plain carbon steels [15], a heat-treated sample was cooled to 150 K and isothermally held for 24 hours. No change of magnetisation was observed, confirming that the martensitic transformation is athermal.

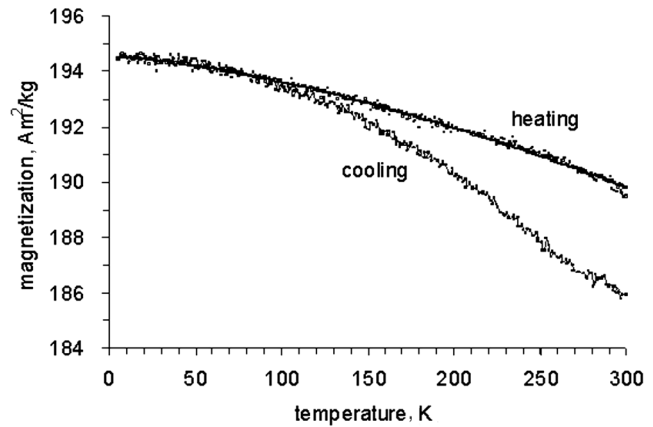


Figure 1. Temperature dependence of mass magnetisation during the first thermal cycle at a magnetic field of 5 T. The dotted line represents a fit to the data using equation (2) with $M_0 = 195 \text{ A}\cdot\text{m}^2/\text{kg}$ and $A = 4.6 \cdot 10^{-6} \text{ K}^{-3/2}$

XRD measurements. To examine the effect of the heat treatment and for comparison with the results from magnetic measurements, XRD measurements were performed. Figure 2 shows the diffractograms of the as-received sample, the heat-treated sample, and the sample after the two thermal cycles. One can see that the as-received (after hot rolling) sample is composed of mainly ferrite (α), while cementite is most likely present but is not detected by XRD due to its small amount [4]. After the heat treatment (intercritical annealing followed by isothermal holding for bainite formation), in addition to ferrite (or bainite) peaks, a significant amount of austenite (γ) was retained. From the integrated peak intensities of austenite and ferrite/bainite, the volume fraction of retained austenite was estimated to be 0.10 [4] and the average carbon concentration in the retained austenite is estimated to be 1.40 mass %. It is noteworthy that only ferrite and austenite were detected by XRD. Other possible phases, such as martensite or cementite, are not detected. This is probably because they are present in too small amounts or their diffraction peaks are overlapped by ferrite or austenite peaks [4]. After two thermal cycles between 300 and 5 K, the austenite peaks nearly disappeared, indicating that austenite transformation has been almost completed. Looking at the profile very carefully, it seems that very small amount of austenite, too small to quantify but less than 1%, remains.

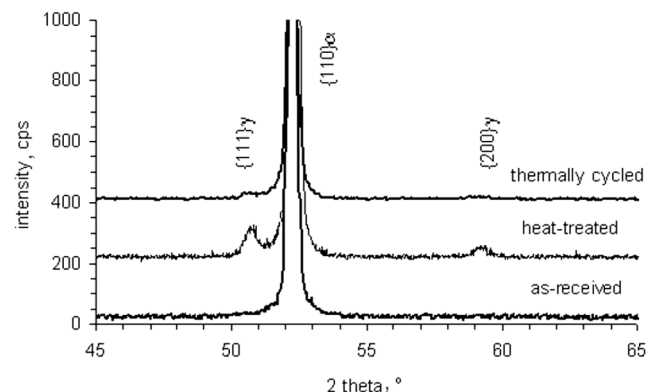


Figure 2. Diffractograms of as-received sample, heat-treated sample and the sample after two thermal cycles. Curves are shifted up 200 cps to separate them

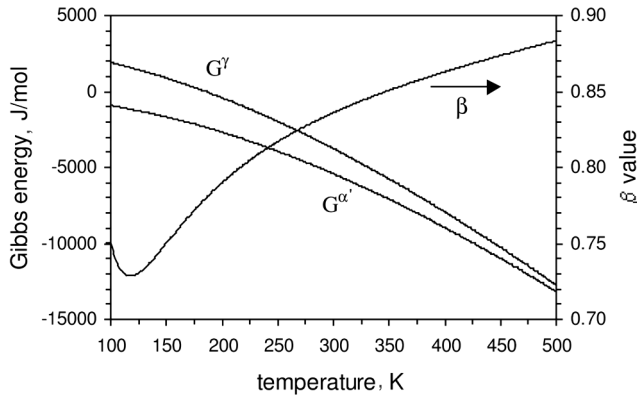


Figure 3. Gibbs free energy of retained austenite (γ) and martensite (α') having a composition of 1.40C-1.52Mn-0.25Si-0.96Al (mass contents in %) and the calculated β values

This remaining austenite could be too stable to transform, due to, for instance, a very small grain size, a very high carbon concentration or a strong compression caused by neighbouring grains.

Thermodynamic analysis. To further analyze the transformation behaviour, the Gibbs free energy (G) of retained austenite and martensite was calculated, as shown in **figure 3**. It is assumed that para-equilibrium is established during the heat treatment. Retained austenite has therefore a composition (mass contents in %) of 1.40C-1.52Mn-0.25Si-0.96Al, where the carbon concentration refers to the XRD results. For temperatures between 100 and 500 K, the Gibbs energy increases almost linearly with decreasing the temperature, which is consistent with the results from literature [5]. However, at temperatures smaller than 100 K, the thermodynamic data become unreliable since the derivative of G - T relation, $dG/dT = -S$ (entropy), increases with decreasing temperature.

From the Gibbs free energy, the chemical driving force for the martensitic transformation, $\Delta G = G^{\alpha'} - G^{\gamma}$, is obtained. If the critical driving force for the start of martensite transformation is taken to be 1260 J/mol [16], the M_s temperature is thus calculated to be 345 K. Furthermore, it is known that a magnetic field would assist martensitic

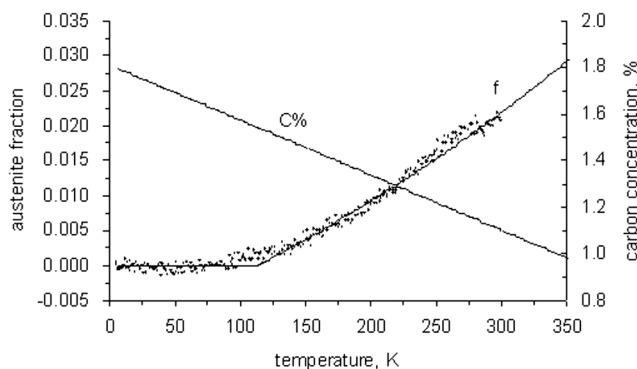


Figure 4. Temperature dependence of austenite fraction during cooling. Dots represent the experimentally determined fraction using equation (3), and the solid line results from equation (1). Carbon concentration (mass contents in %) dependent M_s temperatures are calculated from Andrews' equation

transformation by giving an additional driving force of HM (H : applied magnetic field) [17]. In a constant applied field of 5 T, this additional driving force is about 53 J/mol, which raises the M_s temperature by about 10 K. The M_s temperature is thus expected to be 355 K in a magnetic field of 5 T.

Another important information from the thermodynamic analysis is the calculation of the β values, the ratio of the slopes of the temperature dependence of the Gibbs free energy for martensite (α') and austenite (γ), as requested by Yu's model in equation (1). As presented in figure 3, the β values in the relevant temperature range are around 0.8 and decrease slightly with decreasing temperature.

Temperature dependence of austenite fraction. From the magnetisation measurements and XRD measurements, one may conclude that nearly all retained austenite transforms to austenite after cooling, i.e. $f^{\gamma} \approx 0$ during heating. Furthermore, one can also understand that the volume fraction of ferrite remains unchanged during the thermal cycle, i.e. $f^{\alpha} = \text{constant}$. Denoting b as the ratio of the magnetisation of martensite (α') and ferrite (α), $b(T) = M^{\alpha'}/M^{\alpha}$, the temperature dependence of the austenite fraction during cooling can be estimated by:

$$f^{\gamma} = \frac{M_h - M_c}{M^{\alpha'}} = \frac{M_h - M_c}{M_h} \cdot \frac{b + (1-b)f^{\alpha}}{b}, \quad (3)$$

where the subscripts h and c represent heating and cooling. The ratio b is here taken as 0.90, which is the literature data for an Fe-1.40C (mass contents in %) steel at room temperature [14]. f^{α} is estimated to be 0.85. Therefore, the remaining austenite fraction as a function of temperature can be calculated, as shown by dots in **figure 4**. The austenite fraction decreases with decreasing the temperature as the transformation proceeds till the M_f temperature. However, the initial austenite volume fraction at 300 K is only 0.023, which is much lower than that obtained from the XRD measurements ($f^{\gamma} = 0.10$). The reason for this discrepancy is presently unclear.

From the thermodynamic results, M_s temperature and the β values are known, and temperature dependent austenite fraction can thus be reproduced by the following equation, which is modified from equation (1):

$$f^{\gamma} = f_0^{\gamma} \left(1 - \frac{M_s - T}{M_s - \beta M_f - (1 - \beta)T} \right). \quad (4)$$

where f_0^{γ} is the austenite fraction at M_s . The predicted fraction is presented by a solid line in figure 4, which fits reasonably well with the fraction from the thermomagnitisation measurements for $M_f = 114$ K. If the f^{γ} - T curve in figure 4 calculated by equation (4) is extrapolated to the M_s temperature, one can obtain that the initial austenite at the end of bainitic holding is 0.035.

On the other hand, it is known that the thermal stability of retained austenite is closely related to its carbon con-

centration. Using Andrews' empirical equation [18] ($M_s = 766 - 425 \cdot \%C$, in K), the M_s temperature of individual retained austenite grains is calculated and plotted in figure 4. One can interpret that the temperature dependent austenite fraction is a result of martensitic transformation, in which the austenite grains with lower carbon concentration have less thermal stability and transform first during cooling. This results in the observation that the carbon mass contents in the retained austenite grains vary within the range between approximately 1.10 and 1.55 %.

Conclusions

The thermal stability of retained austenite in a TRIP steel was investigated by thermo-magnetisation measurements, XRD measurements and thermodynamics analysis. The main conclusions are as follows:

- almost all austenite transforms to martensite by cooling down to 5 K, while the M_s and M_f temperatures are 355 K and 114 K, respectively;
- the temperature dependent austenite fraction determined from the thermo-magnetic measurements fits well with the prediction based on Yu's thermodynamic model, and the thermal stability of retained austenite is interpreted from a view point of the carbon concentration in individual austenite grains;
- a discrepancy between the austenite fraction from the XRD measurements and the magnetic measurements exists and will be a subject for further study.

References

- [1] *Matsumura, O.; Sakuma, Y.; Takechi, H.*: Scripta Metall. 21 (1987) p. 1301/06.
- [2] *Sugimoto, K.; Kobayashi, M.; Hashimoto, S.*: Metall. Trans. 23A (1992), p. 3085/91.
- [3] *Chen, H.C.; Era, H.; Shimizu, M.*: Metall. Trans. 20A (1989), p. 437/45.
- [4] *Zhao, L.; van der Pers, N.M.; Sietsma, J.; van der Zwaag, S.*: to be published.
- [5] *Haidemenopoulos, G.N.; Vasilakos, A.N.*: J. Alloys & Compounds 247 (1997), p. 128/33.
- [6] *Yu, H.Y.*: Metall. Mater. Trans. 28A (1997), p. 2499/506.
- [7] *Dođan, A.; Havvatođlu, Y.; Arslan A.*: Eur. Phys. J. AP 15 (2001), p. 79/84.
- [8] *Zhao, L.; Sietsma, J.; van der Zwaag, S.*: Phase transformations and microstructural evolution in aluminum-containing TRIP steels, [in:] Proc. Euro. Conf. on Mater. Sci., Vol. 7, Steels and Materials for Power Plants, [ed.:] P. Neumann et al., Wiley-Vch, Weinheim, 2000, p. 77/82.
- [9] *Zhao, L.; van Dijk, N.H.; Brück, E.; Sietsma, J.; van der Zwaag, S.*: Mat. Sci. Eng. 313A (2001), p. 145/52.
- [10] *Jatczak, C.F.; Larson, L.A.; Shin, S.W.*: Retained Austenite and its Measurements by X-ray Diffraction, Society of Automotive Engineers Inc., Warrendale, Jan. 1980.
- [11] *Cullity, B.D.; Stock, S.R.*: Elements of X-ray diffraction, 3rd edn., Prentice-Hall Inc., Upper Saddle River, 2001, p. 376, p. 626.
- [12] *Kittel, C.*: Introduction to Solid State Physics, 6th edn., John Wiley & Sons Inc., New York (1986), p. 429.
- [13] *Arrott, A.S.; Heinrich, B.*: J. Appl. Phys. 52 (1981) No. 3, p. 2113/15.
- [14] *Bozorth, R.M.*: Ferromagnetism, D. van Nostrand Co. Inc, New York, 1951, p. 368, p. 713.
- [15] *Borgenstam, A.; Hillert, M.*: Acta Mater. 45 (1997) No. 2, p. 651/62.
- [16] *Porter D.A.; Easterling, K.E.*: Phase transformations in metals and alloys, 2nd edn., Chapman & Hall, London, 1992, p. 387.
- [17] *Shibata, K.; Shimozone, T.; Kohno, Y.; Ohtsuka, H.*: Mater. Trans. JIM 41 (2000) No. 8, p. 893/901.
- [18] *Andrews, K.W.*: Journ. Iron Steel Inst. (1965) No. 7, p. 721/27.