Note

Separation of Static Recrystallization and Reverse Transformation of Deformation-induced Martensite in an Austenitic Stainless Steel by Calorimetric Measurements

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1. Introduction

During plastic deformation of metals and alloys a small fraction, between 1 and 5%, of the energy employed in cold working, is stored inside the material in the form of defects, mainly dislocations.[1–3] This stored energy derived from cold working is the driving force for recrystallization and is released during annealing. Despite recrystallization presents one of the smallest driving forces amongst the solid state transformations, for highly deformed metals, measuring stored energy due to deformation can be assessed by calorimetric methods.[4–6]

For austenitic stainless steels (ASSs), depending on steel composition and processing variables, plastic deformation apart from introducing crystal defects, can also cause the appearance of deformation-induced martensites,[7–24] DIM, which has an important influence on the strain-hardening coefficient and on the formability. Two types of martensite may occur in the ASSs, namely: α'-(bcc, ferromagnetic) and ε-(hcp, paramagnetic). Some researches[9,12] show that for low deformation levels the amount of ε-martensite is predominant in relation to α'. When the quantity of α' grows continuously with the degree of deformation, the amount of ε-martensite goes through a maximum and lowers thereafter, suggesting the following transformation sequence: $\gamma \rightarrow \varepsilon \rightarrow \alpha'$.

Reversion of α'-martensite of the DIM in the ASS is less studied than its formation. A good judgment about the thermal stabilities of the ε- and α'- martensites, as well as the deformation bands introduced by cold working, can be obtained from the work of Singh.[16] He detected that during annealing (with duration of 1 h) of a cold rolled AISI 304, ε-martensite remained stable up to 200°C, that α' was stable up to 400°C, whereas deformation bands stayed in non-recrystallized regions up to 800°C. Guy and co-authors[25] studied the reversion of α' induced by cooling and by deforming in two different steels (18%Cr–8%Ni and 18%Cr–12%Ni). In both cases, after 2 min at 600°C, practically all α'-martensite reverted to austenite. Martins and co-authors[26] studied reversion of α'-martensite in the 304 and 304L steels and concluded that the reversion temperature was little sensitive to the type of steel, strain and the effect of precipitation treatments introduced prior to cold working. For the 12 studied conditions (2 steels×2 pretreatments and 3 strain levels), the temperature (annealing for 1 h) for 50% α' ($T_{50\%RM}$) reversion was always within the 550±20°C range. Tavares and co-authors[27] studied reversion of α'-martensite and observed that the $T_{50\%RM}$ depended only slightly on strain and heating rate. The temperatures, measured for 3 levels of strain and 3 heating rates, stayed between 549 and 573°C. Analysis of the above mentioned works[16,25–27] shows that reversion of the strain induced martensites in the ASS occurs at temperatures much lower than the recrystallization temperature, despite the complete reversion of α'-martensite, may reach temperatures of the order of 750°C.

The main objective of this work is to verify if it is possible to separate, with the help of calorimetry, the phenomena of reversion of deformation-induced martensite and recrystallization in a AISI 304 cold worked austenitic stainless steel.

2. Experimental Procedure

Samples of AISI 304 were received as sheets with 1.5 mm thickness. The final processing stages were cold rolling followed by annealing. Chemical composition is given in **Table 1**.

Samples were initially solution annealed at 1 100°C for 1 h followed by water cooling. After solution annealing, steels AISI 304 presented an average grain size of 157 μm. The samples were cold rolled with reductions of 10 to 60%. The samples having a 60% cold reduction were subsequently annealed at temperatures of 500, 550, 650, 700, 750, 850, 900, 950, and 1 000°C for 1 h. Samples having a 60% cold reduction were also submitted to 12 isothermal annealing cycles at 750°C with times ranging from 5 min to 24 h.

Two rolling mills were used in this work. For the determination of the work hardening curves (hardness versus thickness reduction) and the α'-martensite formation curves (α'-martensite % *versus* thickness reduction) a precise laboratory rolling mill was used. On the other hand, for the annealing experiments the specimens were cold rolled in an industrial equipment. Both equipments produced different amounts of α'-martensite, for the same level of cold work.[26]

Several complementary microstructural analysis techniques were employed: optical microscopy (OM), scanning electron microscopy (SEM), energy dispersive analysis (EDX), transmission electron microscopy (TEM), X-ray diffraction (XRD), phase magnetic detection (PMD) and hardness measurements. X-ray diffractions were obtained with a diffractometer with a CuK$_{\alpha 1}$ (λ=0.15405 nm) radiation. Determination of eventual magnetic phases, in the present case α'-martensite, was done on a Fisher ferritoscope. This equipment has a 0.1% ferrite detection limit. Hardness

Table 1. Chemical composition of AISI 304 (wt%).

	C	Cr	Ni	Mn	Si	N	P	S
AISI 304	0.065	18.12	8.37	1.35	0.48	0.0464	0.025	0.002

measurements, used in the determination of hardening and softening curves, were made with a 10 kg load. These techniques are described elsewhere[26] in detail.

A cold worked sample was annealed non-isothermally in a differential scanning calorimeter (DSC). A 100 mg sample was heated between 25 and 1 000°C at a heating rate of 20 K/min in argon. During testing, the DSC measurement was repeated in form of a second run, *i.e.* immediate repetition, since reversion of deformation-induced martensite and recrystallization are irreversible and that the heat flux difference between two consecutive runs eliminates all other contributions that may cause signal noises, hence imbalance to the calorimeter.[6]

3. Results and Discussion

Figure 1 shows the Vickers hardness variation (Fig. 1(a)) and the % α'-martensite (Fig 1(b)) with thickness reduction.

No ε-martensite (HCP, non-magnetic) was detected in the present work. An explanation for this is that at the high strains employed, ε-martensite, that might be eventually formed, would be already transformed to α'-martensite.

Figure 2 presents the softening curves (Fig. 2(a)) and the reversion of α'-martensite (Fig. 2(b)) of the samples that were 60% reduced in thickness and that have been through isochronous annealing (1 h at different temperatures). In Fig. 2(a) it is possible to observe that the 50% softening temperature is situated about 700°C. As this steel has a low stacking fault energy, it is reasonable to suppose that recovery has a small contribution to softening and that 50% softening corresponds approximately to 0.5 fractional recrystallization.[28] From Fig. 2(b) it is possible to determine a 50% reversion temperature ($T_{50\%RM}$): about 550±20°C. This temperature range is below the recrystallization temperature. Furthermore, its kinetics is faster than the recrystallization. For example, at 750°C, the α'-reversion was nearly complete after 5 min treatment.

Figure 3 presents the obtained DSC curves, from which one endothermic and two exothermic peaks may be observed (upper curve). The endothermic peak, situated between 470 and 550°C can be attributed to the reversion of α'-martensite (see Fig. 2(b)) into austenite. The second exothermic peak, situated between 660 and 850°C, can be attributed (see Fig. 2(a)) to recrystallization. The first exothermic peak presents a minimum about 590°C, may be caused by chromium carbide precipitation reactions. Once the sample reaches 1 000°C and cools to room temperature, the same sample is reheated (second run) under the same conditions (lower curve) and no peaks have been observed this time. This implies that the peaks observed in the first run are truly related to the elimination of martensite and elimination of crystal defects and possibly to precipitation reactions.

Analyzing the endothermic peak, attributed to the reversion of α'-martensite, the energy associated to martensite reversion may be evaluated. If we consider that only about 12% martensite (from Fig. 2(b)) has been reverted to austenite, we can estimate (from Fig. 3) that the energy due to the $\alpha' \rightarrow \gamma$ reversion is about 8 J/g (440 J/mol). Despite that enthalpies of martensite reversion in austenitic stainless steels have not been found in the literature, some related
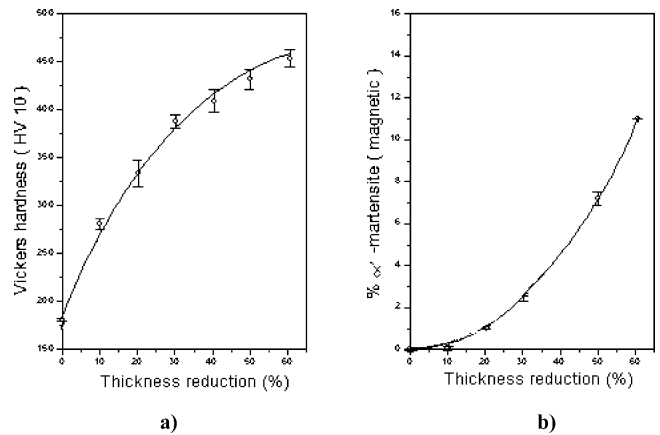
Fig. 1. Cold deformation of AISI 304 steel: (a) Vickers hardness versus thickness reduction; (b) martensite % *versus* thickness reduction.[26]
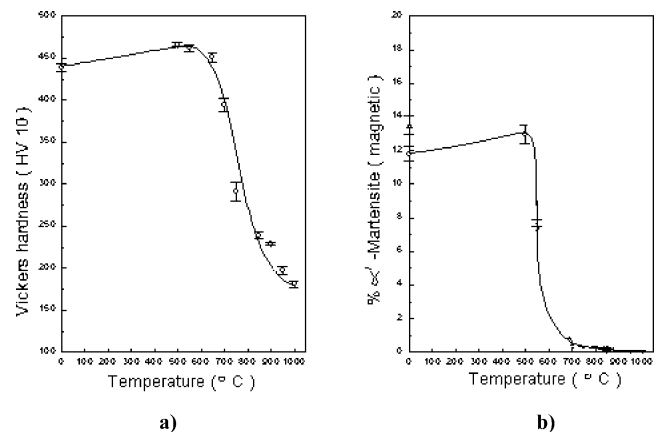
Fig. 2. Annealing of 60% cold-worked AISI 304 steel: (a) softening curve (Vickers hardness *versus* annealing temperature, -1 h); (b) martensite reversion curve (% martensite *versus* annealing temperature, -1 h).[26]
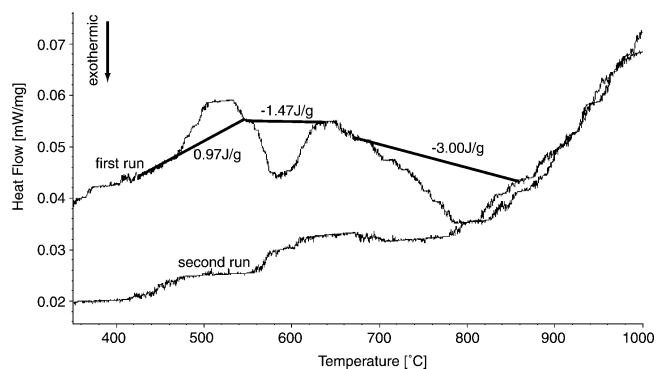
Fig. 3. Heat flow curves (DSC measurements) of two consecutive runs at 20 K/min for the AISI 304 steel, after 60% thickness reduction.

values may be used as a base for comparison. If we consider the work of Orr and Chipman[29] it may be observed that the latent heat of the phase transformation $\alpha \rightarrow \gamma$ of pure iron at 912°C is 900 J/mol. On the other hand, the work of Lee *et al*.[30] reports that the heat evolved during martensite formation in an Fe–18.5Cr–8.7Ni alloy (in the temperature range of 20 and −117°C) is ~1920 J/mol. Here it must be pointed out that the alloy used in the present work is similar to the austenitic stainless steel mentioned above, yet the

transformation temperature is about 550°C (*i.e.*, between the transformation temperatures mentioned in the literature) and that the reaction direction is similar to the one occurring in pure iron.

The energy associated to the first exothermic reaction (first exothermic peak in Fig. 3) can be attributed to the $(Cr, Fe)_{23}C_6$ precipitation reaction. The temperature of 590°C is somewhat low for the precipitation maximum kinetics, however it has been taken into account that cold deformation of the solution annealed steel enhances precipitation.[31,32] The heat of formation for $Cr_{23}C_6$ is much higher than the one for the other two reactions (martensite reversion and recrystallization), but since the precipitated carbide amount is about 1%, the corresponding energy release is consistent with the experimental result of 1.47 J/g.

The energy associated to the second exothermic reaction (second exothermic peak in Fig. 3), which by comparing temperatures of Figs. 2(a) and 3 can be attributed to recrystallization, cannot be evaluated with the same confidence as in the case of the endothermic peak, since the reaction interval is rather uncertainly defined. Thus the amount of about 3 J/g (173 J/mol) for the energy release is an approximation only.

Stored energy values of rolled austenitic stainless steels have not been found in the literature. On the other hand, from the measured mechanical data of the steel (Fig. 1(a)) the stored energy can be estimated.

Using the approximate relationship[33] that relates flow stress (σ) to the Brinell hardness (HB):

$$\sigma \approx 3.45 \, HB \quad\text{.................................}(1)$$

both given in MPa, and taking into account that Vickers hardness (HV 10) is nearly identical to the Brinell hardness, we can transform the hardness versus thickness reduction curve of Fig. 1(a) into a flow stress versus thickness reduction curve. The relationship between flow stress (σ) and dislocation density (ρ) of the form:

$$\sigma = \alpha G b \, (\rho)^{1/2} \quad\text{................................}(2)$$

where α is a constant of the order of 0.5 and G and b are shear modulus and Burgers vector is well known. Equation (2) has been shown[34] to hold for a wide variety of materials. Further, an additional approximate relationship between stored energy (E_{Stor}) and the dislocation density can be used[3]:

$$E_{Stor} = \beta G b^2 \rho \quad\text{................................}(3)$$

where β is a constant of the order 0.5.

Combining Eqs. (2) and (3) we get:

$$E_{Stor} = (\beta/\alpha^2)(1/G)\sigma^2 \quad\text{..........................}(4)$$

In Eq. (4) σ is the increment of flow stress due to dislocations produced by cold rolling. Using the experimental data of Fig. 1(a):

$$\sigma = \sigma \text{ (for 60\% thickness reduction)}$$
$$-\sigma \text{ (for 0\% thickness reduction)}$$
$$= 918 \text{ MPa}$$

and $G = 75 \times 10^3$ MPa[35] a value of $E_{Stor} = 2.9$ J/g (160 J/mol) is obtained. Thus the calorimetrically determined amount of energy release during recrystallization and the value of

stored energy due to dislocations produced by cold rolling are in good agreement.

REFERENCES

1) M. B. Bever, D. L. Holt and A. L. Titchener: Progress of Materials Science, Vol. 17, Pergamon Press, Oxford, (1973), 1.
2) H.-P. Stüwe: Recrystallization of Metallic Materials, ed. by F. Haeßner, Dr. Riederer Verlag, Stuttgart, (1978), 11.
3) F. J. Humphreys and M. Hatherly: Recrystallization and Related Annealing Phenomena, Pergamon Press, Oxford, (1996), 11.
4) F. Haeßner: Recrystallization '90, ed. by T. Chandra, TMS, Warrendale, PA, (1990), 511.
5) F. Scholz, J. H. Driver and E. Woldt: *Scr. Mater.*, **40** (1999), 949.
6) F. Scholz and E. Woldt: *J. Therm. Anal. Calor.*, **64** (2001), 895.
7) P. L. Mangonon Jr. and G. Thomas: *Metall. Mater. Trans.*, **1** (1970), 1577.
8) G. B. Olson and M. Cohen: *Metall. Trans.*, **6A** (1975), 791.
9) V. Seetharaman and R. Krishnan: *J. Mater. Sci.*, **16** (1981), 523.
10) S. S. Hecker, M. G. Stout, K. P. Staudhamer and J. L. Smith: *Metall. Trans.*, **13A** (1982), 619.
11) L. E. Murr, K. P. Staudhamer and S. S. Hecker: *Metall. Trans.*, **13A** (1982), 627.
12) M. W. Bowkett, S. R. Keown and D. R. Harries: *Met. Sci.*, **16** (1982), 499.
13) K. P. Staudhamer, L. E. Murr and S. S. Hecker: *Acta Metall.*, **31** (1983), 267.
14) K. Takashima, Y. Higo and S. Numomura: *Philos. Mag.* A, **49** (1984), 231.
15) Y. Kaieda and A. Oguchi: *J. Mater. Sci.*, **20** (1985), 1847.
16) J. Singh: *J. Mater. Sci.*, **20** (1985), 3157.
17) D. C. Cook: *Metall. Trans.*, **18A** (1987), 201.
18) G. L. Huang, D. K. Matlock and G. Krauss: *Metall. Trans.*, **20A** (1989), 1239.
19) A. Kumar and L. K. Singhal: *Metall. Trans.*, **19A** (1988), 1021.
20) S. K. Varma, J. Kalyanam, L. E. Murr and V. Srinivas: *J. Mater. Sci. Lett.*, **13** (1994), 107.
21) S. G. S. Raman and K. A. Padmanabhan: *J. Mater. Sci. Lett.*, **13** (1994), 389.
22) A. Weiß, X. Fang, H.-J. Eckstein, C. Eckstein and W. Dahl: *Steel Res.*, **66** (1995), 495.
23) W.-S. Lee and C-F. Lin: *Scr. Mater.*, **43** (2000), 777.
24) J.-Y. Choi and W. Jin: *Scr. Mater.*, **36** (1997), 99.
25) K. B. Guy, E. P. Butler and D. R. F. West: *Met. Sci.*, **17** (1983), 167.
26) L. F. M. Martins, R. L. Plaut and A. F. Padilha: *ISIJ Int.*, **38** (1998), 572.
27) S. S. M. Tavares, D. Fruchart and S. Miraglia: *J. Alloys Compounds*, **307** (2000), 311.
28) H.-P. Stüwe, A. F. Padilha and F. Siciliano, Jr.: *Mater. Sci. Eng.*, **A333** (2002), 361.
29) R. L. Orr and J. Chipman: *Trans. AIME*, **239** (1967), 630.
30) B. Lee, S. Millman, I. L. MacDougall, S. R. Keown and B. B. Argent: *Met. Sci.*, **11** (1977), 261.
31) A. F. Padilha and P. R. Rios: *ISIJ Int.*, **42** (2002), 325.
32) A. F. Padilha, R. L. Plaut and P. R. Rios: *ISIJ Int.*, **43** (2003), 135.
33) W. D. Callister, Jr.: Materials Science and Engineering, 5th Ed., John Wiley & Sons, Inc., New York, (2000), 139.
34) R. J. McElroy and Z. C. Szkopiak: *Int. Metall. Rev.*, **17** (1972), 175.
35) ASM Specialty Handbook: Stainless Steels, ed. by J. R. Davis, ASM International, Materials Park, OH, (1994), 489.