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A study of the reverse martensitic transformations in austenitic stainless steels by calorimetry and isothermal heat treatments

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ABSTRACT

The objective of this work was to study the reversion of the strain-induced α-martensite to γ-austenite in three sets of AISI 304, 316-L and 347 stainless steels specimens. To obtaining a high amount of α'-martensite ($\gamma \rightarrow \alpha'$), the samples were submitted to 63% reduction in thickness by cold rolling at a temperature of –70 ºC. The reversion of martensite to austenite was made by means of 1-hour isothermal heat treatments between 200 and 1000 ºC ($\alpha' \rightarrow \gamma$). Martensite amounts were determined by measurements made with a commercial feritscope. The main analysis of reversion was performed by differential scanning calorimetry (DSC) studies with heating rates of 10, 20 and 40 °C/min. It was determined that under continuous heating the deformation-induced reversion is carried out by a superposition of the diffusional and shear mechanisms, for the heating rates tested. The reversion begins via diffusion-controlled mechanism at temperatures between 414 and 453 °C and ends via non-diffusional mechanism between 557 and 633 °C. On the other hand, the energy per unit mass of the transformation turned out to be between 37 and 63 J/g; and it was found that this depends on the heating rate.

Keywords: α'-martensite; reversion; austenitic stainless steel; calorimetry; isothermal-treatments.

1. INTRODUCTION

The austenitic stainless steels of the 300 series are metastable, the γ-austenite phase can transform to ε-martensite and to α'-martensite phases due to cold plastic deformation. The most likely phase transformation is from γ-austenite (fcc, paramagnetic) to α'-martensite (bcc or bct, ferromagnetic), deformation-induced martensite (DIM). The strain-induced martensitic transformation enhances the work hardening of these stainless steels and affects their ductility. The amount of α'-martensite obtained depends on the chemical composition, the process temperature and the strain applied. The austenite can be recovered with subsequent heat treatments. Likewise, the amount of recovered austenite depends on the chemical composition of the steel, temperature, time and rate of heat treatment [1, 2].

The martensite to austenite reversion process in austenitic stainless steels has been studied since the 1970's and 1980's, intensively in the Japan in 1990's and a further academic interest has appeared later 2005–2020; JÄRVENPÄÄ *et al.* [3] present an exhaustive review of works that involve the formation of martensite by cold rolling and the reversion process by annealing. This more recent interest in the reversal transformation of α'-martensite has received interest due to the possibility of controlling the microstructure to obtain fine or ultrafine grain size in austenitic stainless steels [4–9]; or to produce localized areas of austenite in a martensitic structure to achieve good formability while maintaining high mechanical strength [10, 11].

The result of the reversion reaction depends on multiple factors: steel grade, deformation that caused the DIM, α' percentage before reversion HT, temperature and duration of the annealing, and heating rate. There are basically two types of mechanisms proposed for DIM reversion: diffusional and shear (non-diffusional) [12–14]. The occurrence of one or the other depends mainly on the chemical composition of the steel, on the heating rate and on the temperature and duration of the HT (in the case of isothermal treatments) [12, 15, 16]. Two of the parameters obtained from the DSC tests are the start and end temperatures of the reversion from martensite to

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austenite. These temperatures are identified as A_s and A_f when the mechanism is diffusional, and with primes at the same temperatures when the process is diffusionless (A'_s and A'_f). Figure 1 is a schematic representation of the results obtained in [15, 16] and its purpose, in this case, is to show how the start and end temperatures of the reversion reaction depend on the heating rate. According to these authors, there are two regions, denoted as I and II, separated by a heating rate value that depends on the steel and is represented by the vertical dotted line in Figure 1. For example, in LEEM, *et al.* [15] they find that this separation rate is 10 °C/s (600 °C/min), for a cold rolled steel Fe-13%Cr-7%Ni-3%Si; while in HAN and LEE [16] for a steel also cold rolled Fe-(5–9%)Mn-0.05%C, the separation heating rate resulted 15 °C/s (900 °C/min). In Region I, reversal start and end temperatures tend to increase as the heating rate increases; this indicates that reversal reaction occurs diffusionally or by an overlap of both mechanisms (diffusional and shear) [12, 15–17]. Then, in region II it is observed that the temperatures of beginning and ending tend to remain constant, which means that the reversal occurs only via shear mechanism, since at such high heating rates there is no time for diffusion.

α'-martensite reversion reaction was studied in a set of cold-rolled AISI 304 steels samples in TAMURA [18]. These authors applied thermomagnetic analysis of continuous heating between 100 and 800 °C with speeds of 2, 5 and 10 °C/min and isothermal treatments between 250 °C and 560 °C. Thermomagnetic tests showed A_s values in the range 433–445 °C and A_f in the interval 694–724 °C. They do not identify these reversal start and end temperatures with any particular mechanism; but from observing that the α' amount decreases by keeping the temperature constant at 560 °C during one of the continuous heating treatments, they point out the transformation can progress diffusionally once it has started.

The reverse transformation $\alpha' \rightarrow \gamma$ has also been studied by GUY *et al.* [19] for two austenitic stainless steels: Fe-18%Cr-8%Ni and Fe-18%Cr-12%Ni. DIM was induced by two methods: rolling at –196 °C, and cooling to –196 °C with a 30 min holding time. Reversion to austenite was carried out by rapid heating using a salt bath. The times and temperatures studied were 2 and 30 min between 200 and 900 °C, and up to 10000 min (167 horas) at 550°C.They determine the values of A_s and A_f: 540 and 650 °C for 8/18; and 470 and 610 °C for 12/18; with an uncertainty of 10°C. They postulate that the reverse transformation between A_s and A_f occurs by shear mechanism and then continues as diffusional.

By thermodynamic analysis TOMIMURA *et al.* [20], analyze the Gibbs free energy change between α-ferrite and γ-austenite ($\Delta G^{\alpha-\gamma}$) for a ternary Fe-Ni-Cr system as a function of temperature and chemical composition, they study 16Cr-10Ni and 18Cr-9Ni steels. When the value of $\Delta G^{\alpha-\gamma} < 0$, γ is more stable than α, which occurs from approximately 450 °C for these steels. The temperature at which $\Delta G^{\alpha-\gamma} = 0$, is called by them T_0, therefore, $T_0 \approx 450$ °C. However, for the reversion to be carried out via shear mechanism, an additional driving force is necessary. They experimentally determined that for α'-martensite to revert to austenite via shear mechanism, in a 90% cold rolled 16Cr-10Ni steel, the minimum temperature must be 650 °C, they call T_1 at this temperature. Reversion treatments of deformation induced α' were carried out using a salt bath which enables rapid heating (18000 °C/min) to annealing temperatures between 450 and 750 °C, for 10 s, 10 min or 16.7 h; T_1 was determined with these HT. They observed that from 650 °C the reversal process became independent of the annealing time (and the reverse transformation begins by shear mechanism), while at lower temperatures there was a dependence on it. TOMIMURA *et al.* [20], also calculate T_1 for 18Cr-9Ni steel: for the reversal to be started via shear mechanism, a temperature of at least 750 °C is needed. If, on the other hand, annealing is carried out at 650 °C, the reversal would be diffusional, since at this temperature the driving force necessary for the shear reversion would not be reached, in 18Cr-9Ni steel.

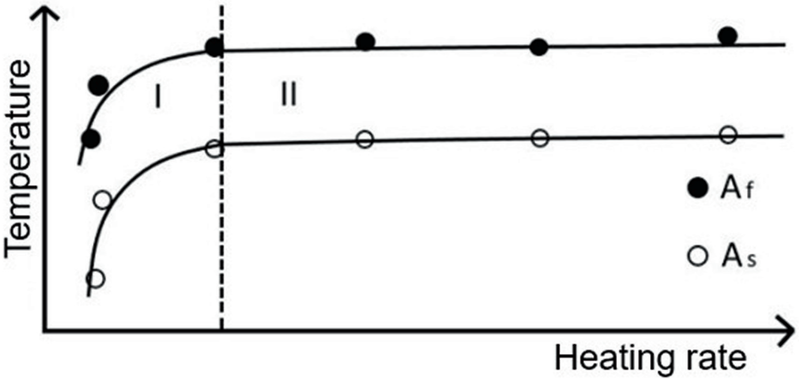

Figure 1: A_s and A_f dependence on heating rate.

In this paper the reversion of the strain-induced α'-martensite to γ-austenite was studied in three sets of AISI 304, 316L and 347 stainless steels. The objectives of this research were to know the temperature range in which the reversion transformation occurs, as well as to determine the amount of the different phases. For this study, DSC test and reversion isothermal heat treatments were considered. The temperature at the beginning and end of the reversion, the energy of the transformation and the amount of each of the phases present after isothermal reversion treatments were determined. Besides, these assays allowed us to study the reversion mechanisms present during the transformation: diffusional and shear.

2. MATERIALS AND METHODS

2.1. Materials

Three sets of austenitic stainless steels samples were used for this research: AISI 304, AISI 316L and AISI 347, [21, 22]; their Wt % compositions are shown in Table 1. The samples were prepared in the same way as those studied in [23–25]. First, they were submitted to one-hour austenitization annealing at 1050 °C in vacuum and cooled in air. All specimens were subsequently 63% cold rolled at –70 ºC (203 K) to induce $\gamma \rightarrow \alpha'$ phase transformation, producing a high proportion of martensite, about 80%. This was the initial condition for the studies of the reversion of martensite. The cold-rolled specimens ($65 \times 30 \times 2.3$ mm^3) were individually submitted to heat treatments (HT) for the partial reversion of the γ phase. These HT consisted of one hour soaking at temperatures between 200 and 1000 °C. The maximum heating rate for these HT was estimated to be around 1100 °C/min, the lower HT temperature the lower heating rate. In this way, the austenitic γ phase was partially recovered back in different quantities for each specimen, thus obtaining series of two-phase specimens with different martensite contents. The phases present in the specimens were identified by XRD. Concentrations of α'-martensite were quantified by measurements made with a commercial ferritoscope FischerÒ Feritscope FMP30, by using a calibration curve presented in FAVA *et al.* [22] and updated in SALGADO [21]; this calibration curve converts the measurements of Wt % δ-ferrite into Wt % of α'-martensite.

2.2. M_{d30}

Austenitic stainless steels are susceptible to martensite transformation when they are subjected to cryogenic treatments below a certain temperature called M_S, at this temperature the driving force reaches the critical value $\Delta G_{M_S}^{\gamma \rightarrow \alpha'}$, which is the minimum required for spontaneous martensitic transformation to happen. However, if an adequate mechanical driving force U' is applied to austenite, martensitic transformation can occur at a temperature T_1, higher than M_S; since $\Delta G_{T_1}^{\gamma \rightarrow \alpha'} + U' = \Delta G_{M_S}^{\gamma \rightarrow \alpha'}$. When a mechanical driving force is involved in transformation, it is classified into two types: stress-assisted martensitic transformation and deformation-induced martensitic transformation. The first involves elastic deformations and occurs at low temperatures; (but above M_S). The second takes place in the case of plastic deformations and higher temperatures, e.g., room temperature [1, 26, 27]. In the latter, martensitic transformation is related to energetically favorable nucleation sites generated by plastic deformation [26]. In the case of austenitic stainless steels, it has been shown that the DIM nucleation sites are located at the intersections of two shear bands by the aid of piled-up dislocations and at obstacles such as grain boundaries and twinning boundaries [18, 26, 28–30]. Temperature is crucial in deformation-induced transformation, just as it is for spontaneous transformation. Transformation is enhanced by the decrease in temperature [31, 32]; in HECKER *et al.* [31] the authors analyze results of the amount of DIM as a function of the traction strain in a 304 stainless steel and observe an increase in DIM as the temperature decreases. For example, with a true strain of 0.40: at 22 °C it forms around 10% volume fraction of α', at 10 °C 43%, at 0 °C almost 60%, at –30 °C around 80%; and for –30 °C, –70 °C and –188 °C the amount of α' appears to saturate at about 85%, for the highest true strains. Since the transformation occurs above M_S, the stability of these steels is classified by other temperatures. One of them is M_d, which is the limit temperature above which there will be no martensitic transformation induced by deformation due to the application of plastic deformations. However, as this temperature is difficult to measure, ANGEL [33] established another one: M_{d30} (known also as $M_{d(30/50)}$).

Table 1: Chemical compositions of the stainless steels in Wt %.

AISI	Fe	C	Si	Mn	P	S	Cr	Ni	Mo	Nb
304	Balance	0.04	0.68	1.69	0.022	0.005	18.8	9.2	0.08	–
316 L	Balance	0.02	0.39	1.50	0.023	0.010	17.9	12.3	2.48	<0.01
347	Balance	0.03	0.52	1.55	0.018	0.003	17.9	9.3	0.22	0.60

Table 2: M_{d30}.

AISI	AISI 304	AISI 316L	AISI 347
M_{d30} [°C]	28	–20	44

It is the temperature for which 50% martensite is formed by applying 30% true strain, in a tensile test. M_{d30} is a good measure of metastable stainless steels stability and is determined by the chemical composition, as stated in the empirical ANGEL formula: M_{d30} (°C) = 413 – 13.7(%Cr) – 9.5(%Ni) – 8.1(%Mn) – 18.5(%Mo) – 9.2(%Si) – 462(%[C+N]). In this equation the elementary fractions are expressed in weight percent, and it indicates that the higher the proportion of alloying elements, the more they improve the stability of austenite. The resulting M_{d30} for the studied steels are presented in Table 2. Because AISI 347 steel has the highest M_{d30}, it is the one with the greatest tendency to form martensite when subjected to deformation at a temperature below M_d and AISI 316L is the one with the least tendency. In addition to the effect of chemical composition, some authors [1, 8] also consider the effects of initial grain size by applying NOHARA's formula NOHARA *et al.* [34]; but here ANGEL's formula was used because all the samples had already been laminated before starting this study, i.e., the initial grain size was not measured before rolling.

2.3. Differential scanning calorimetry

For differential scanning calorimetry studies, the samples that had received the HT at the lowest temperature, 200 °C, were selected. These samples correspond to the first three points in Figure 2 for each of the studied steels; and according to the bibliography the reversal transformation starts between ~400–800 °C [35–37]. A Setaram LabSys Evo differential scanning calorimeter was used.

Thermal cycles from 50 °C to 1400 °C were programmed with heating rates of 10, 20 and 40 °C/min for all samples, and controlled cooling. Two tests were carried out for each sample and rate. The tests were performed in argon atmosphere with a flow of 50 ml/min. The data obtained was processed using the software provided by the calorimeter manufacturer, called "CALISTO Processing". From the analysis of the results the following were extracted: temperature at the beginning of the transformation, temperature at the end of the transformation, and energy of the transformation per unit mass of α'-martensite transformed, for details on data processing see [21].

3. RESULTS

3.1. Reversion heat treatments

The results of the reversion HT are shown in Figure 2. As expected, according to the M_{d30} values, Table 2: AISI 347 steel was the one that formed the highest amount of deformation induced martensite; the amount of α' formed by 304 steel is slightly less than that of 347; while the initial concentration of α' for 316L steel is approximately half the values corresponding to the other two steels.

For steels 304 and 347, between 300 °C and 400 °C, a slight increase in the amount of DIM was observed, during the reversion HT, as shown in Figure 2. Both steels reach the maximum α' concentration around 400 °C: with an increase from 81% to 83% for 304 and from 86% to 88% for 347. This result appears to match the previous peak to the DIM reversal reaction peak in the thermograms obtained from the DSC tests, discussed in the next section. The increase in the amount of α' is one of the hardening mechanisms postulated for cold-formed austenitic stainless steels and then heat-treated in static baths between 250 °C and 450 °C and it is called annealing induced martensitic transformation [1, 19, 36, 38, 39].

3.2. DSC tests

In the DSC tests, all thermograms showed three peaks, Figure 3 highlights them for AISI 347 sample: the endothermic ones (peaks 2) correspond to the reversal transformation of the martensite. As a general observation, it can be said that for the different heating rates a shift of the peaks towards higher temperatures was observed as the heating rate increased.

Literature indicates that the endothermic peaks, analogous to the peaks denoted as 2 in the thermograms of Figure 3, correspond to the reversion reaction $\alpha' \rightarrow \gamma$ [12, 36, 37, 40]. These endothermic peaks were the ones that were studied in detail and quantitatively in this research. Also, these studies were compared with the results of the static HT with which the samples were prepared, Figure 2. Table 3 contains the temperatures at which the endothermic peaks presented their corresponding minimum. For all DSC tests, at all the peaks corresponding to

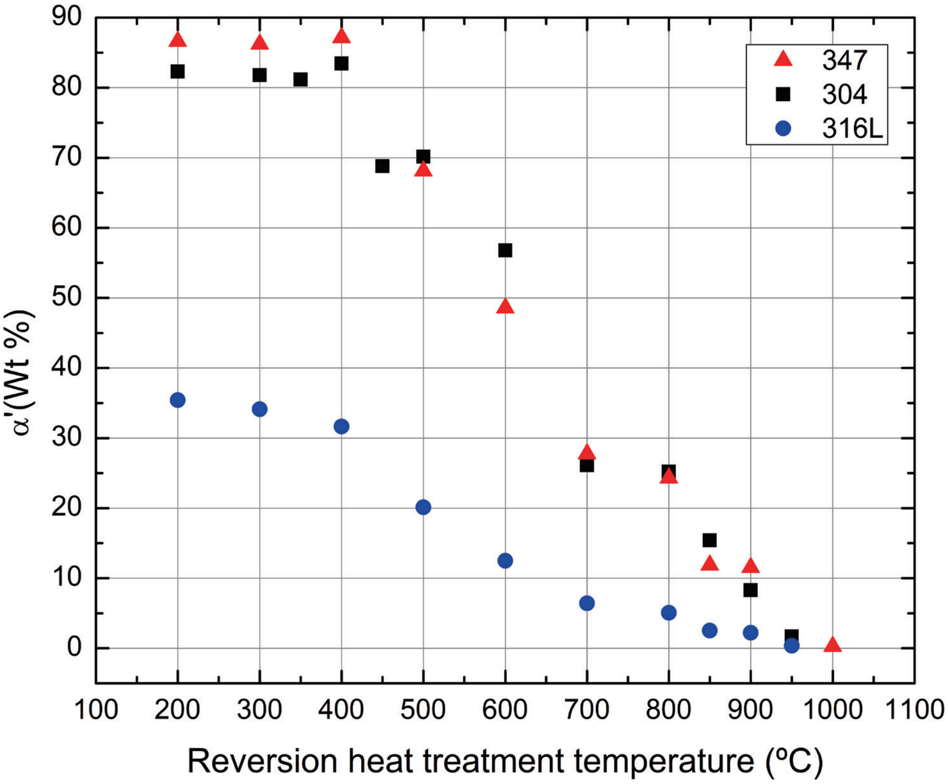

Figure 2: Martensite fraction after reversion HT.

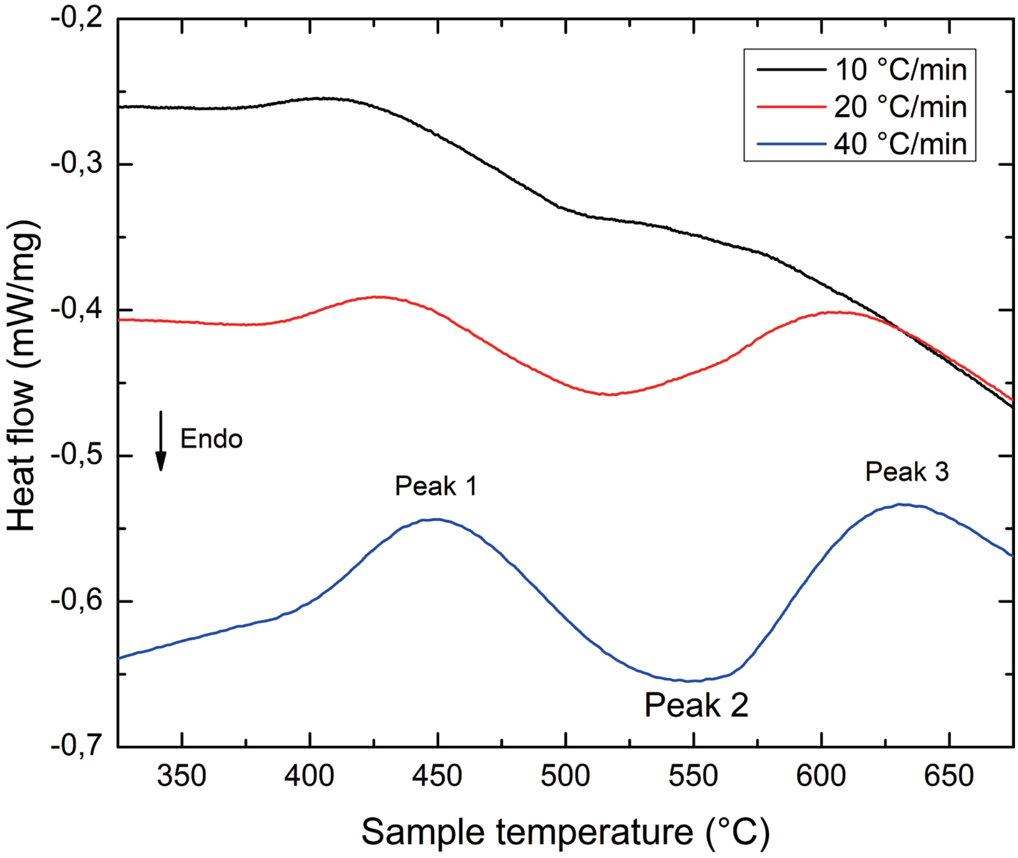

Figure 3: Zoom of the DSC curves for AISI 347 sample (heat treated at 200 °C). Shift of the peaks towards higher temperatures as the heating rate is increasing.

the reversal reaction the peak start temperature was identified as diffusional, $\mathbf{A_s}$, and the ending temperature as non-diffusional, $\mathbf{A'_f}$, as defined in the Introduction. Those A_s and A'_f temperatures were analyzed as a function of the heating rate. As one of the objectives of this work was the study of the reversal reaction of the DIM; for the exothermic peaks, analogous to peaks 1 and 3 of the thermogram of Figure 3, only a brief analysis was carried out based on the consulted bibliography.

Figure 4 plots the start temperatures of the endothermic reaction (A_s) and the temperature of its completion (A'_f) as a function of the heating rates of the DSC tests; Table 4 shows these temperatures. As the heating rate increases, so do the α'-martensite reversal start and end temperatures, and therefore the samples should be in region I of Figure 1.

Table 3: Temperatures where endothermic peaks present the minimum, for each sample and heating rate.

V (°C/MIN)	AISI 304 °C	AISI 316L °C	AISI 347 °C
10	500	488	500
10	498	488	501
20	513	502	524
20	512	501	519
40	540	524	543
40	541	525	540

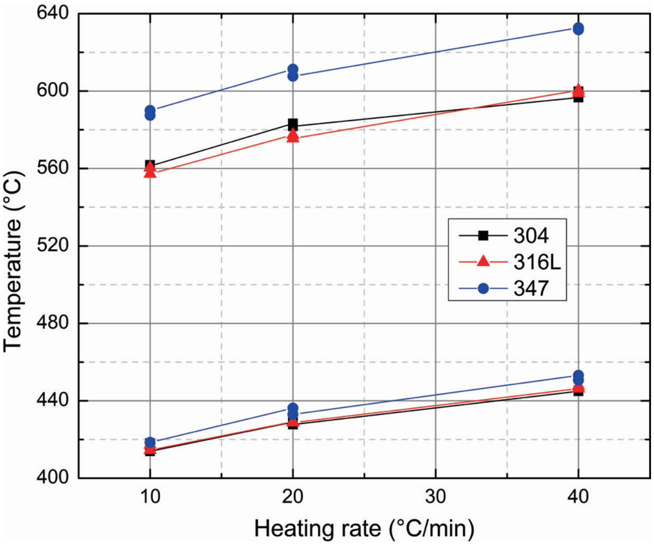

Figure 4: Diffusional reversion start temperatures (A_s, endothermic peak start temperature) and shear reversion finishing temperatures (A'_f, endothermic peak finishing temperature) vs heating rates.

Table 4: Start and end temperatures of the endothermic reaction and heating rates.

V (°C/MIN)	AISI 304		AISI 316L		AISI 347	
	A_s (°C)	A'_f (°C)	A_s (°C)	A'_f (°C)	A_s (°C)	A'_f (°C)
10	418	562	417	560	418	587
10	414	561	414	557	418	590
20	429	583	429	577	436	611
20	428	582	429	575	433	608
40	445	597	446	600	453	633
40	445	600	448	599	451	632

3.3 Transformation energies

Energies per unit mass of α' depending on the heating rate for the DSC tests of this work are presented in Figure 5 and Table 5. In these energies it is not possible to distinguish between energy of the diffusional mechanism and energy of the shear mechanism; and it was observed that the energy per unit mass decreases as the heating rate increases.

4. DISCUSSION

4.1. Diffusion-controlled and shear mechanisms

According to the results, we can assume that the reverse martensitic transformation is initiated by diffusion (for this reason we denote the starting temperatures as A_s). For the three steels, in the conditions of the DSC tests used and considering [12], it can be estimated that the reversion occurred through a superposition of both diffusional and shear mechanisms. This fact is also supported by LEE *et al.* [41], where they state that in continuous heating the shear reversal takes place regardless of the heating rate. Therefore, there would be a certain fraction of α'-martensite that would be reverting to austenite via a non-diffusional mechanism. That is, for the steels and conditions studied here, diffusion-controlled α' reversal begins at the onset of endothermic peaks (between 414 and 453 °C, A_s temperatures in Table 4), and shear reversion would be activated at higher temperatures $A'_s > A_s$ [20]. However, these A'_s temperatures cannot be determined in the experimental conditions of our DSC test, that is, under these conditions the diffusion and shear mechanisms cannot be separated [12]. From bibliographic analysis, it is also assumed that the shear mechanism ends when the endothermic peak ends (between 557 and 633 °C, A'_f temperatures in Table 4) [12, 20]. In addition, the completion temperature of diffusional reversion (A_f) could not be determined under the conditions tested; but it would be at a temperature higher than $A'_f (A_f > A'_f)$.

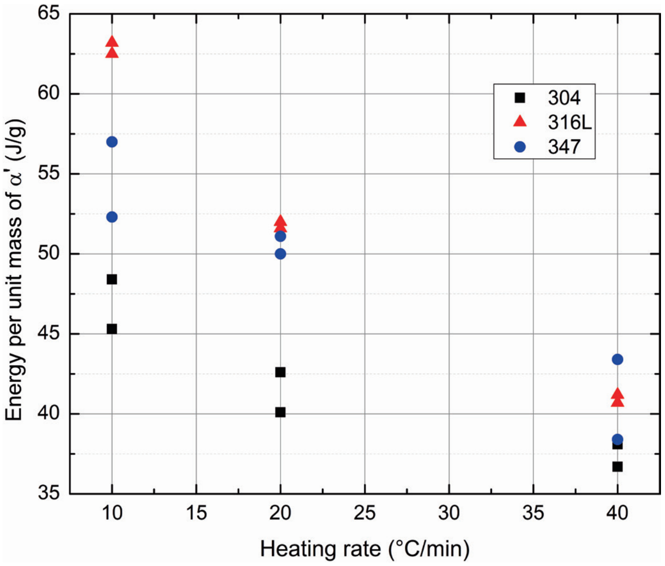

Figure 5: Energy per unit mass of α' as a function of heating rates.

Table 5: Energies per unit mass of α', for the endothermic peaks.

V (°C/MIN)	AISI 304	AISI 316L	AISI 347
	ENERGY (J/g)	ENERGY (J/g)	ENERGY (J/g)
10	45	62	57
10	48	63	52
20	43	52	51
20	40	52	50
40	37	41	38
40	38	41	43

Peak 1, prior to reverse martensitic transformation peak, could be caused by the formation of a small additional amount of α'-martensite [36, 38, 39]; which is consistent with the α' Wt % measurements made on samples of AISI 304 and 347 steels, see Figure 2 and Figure 3. During the reversion HT of AISI 316L steel, this increase in the amount of α'-martensite was not observed, Figure 2. This could be because AISI 316L steel has the highest Ni/Cr rate, of the three steels, and Ni tends to stabilize the γ-phase; or the greater thermal stability of AISI 316L could also be due to the Mo content of this steel [42]. This lower tendency to form martensite also appears in its M_{d30} value, the lowest for the three steels, Table 2. However peak 1 appears; there is no agreed explanation for the increase in the α' amount in the temperature range 300–400 °C [13, 19, 36, 38, 39]: nucleation of new α' particles, growth of the existing α' laths, precipitation of carbides which locally decrease the Cr concentration and increase the M_S, or to segregation and conglomeration of carbon atoms.

Exothermic peak 3 is most likely to be the recovery of the reverse austenitic structure [12], i.e., by a decrease in defect density. But according to studies done on AISI 304 steels [43] and on AISI 301 [12], it could also correspond to the formation of carbides; although our steels have a low C content and in the case of the 347 steel studied, it is stabilized by the formation of Nb carbides.

The hardening behavior of a 40% cold rolled 304 stainless steel containing DIM during static strain ageing was investigated by LEE *et al.* [36]. Particularly, they examined the effect of aging temperature on strength and the amount of α'-martensite. The aging treatments were performed on cold rolled stainless steel sheets in a heated salt bath in the temperature range of 200–700 °C for an hour; they also performed DSC thermal analysis with heating rates between 2 and 16 °C/min. They find that the amount of α'-martensite is increased for the sample aged at 450 °C from 45.5% to 50%; this increase is well known and as mentioned, was also recorded in this work, Figure 2. In the DSC tests, the reversal α' peak is around 500 °C and they postulate that reversion begins after 450°C, so they relate this value to the maximum α'-martensite concentration at that same temperature observed in aging treatments. They also find an endothermic peak prior to the exothermic peak corresponding to the α' reversion, between 350 °C and 450 °C. Authors say that there is no clear explanation of the mechanism corresponding to this peak and that it could be related to one or more microstructural changes, such as additional formation of α'-martensite or recovery of α'-martensite (defects removal). But they also relate this peak to the diffusion of C and Cr atoms into austenite to form fine carbide precipitates which would locally increase M_S and promote the further α'-martensite formation.

Following TOMIMURA *et al.* [20], the temperature at which the isothermal treatment is carried out on the steels would affect the reversion mechanism in the following way: if the temperature of the isothermal treatment is higher than T_0 but less than T_1, see Introduction, the reversion will be diffusional and if the isothermal treatment is carried out at a temperature higher than T_1, the reversion will occur via the non-diffusional mechanism. These conclusions could be applied to our AISI 304, 316L and 347 steels; but it must be kept in mind that in TOMIMURA *et al.* [20] the presence of other alloy elements is not considered and also our heating rates involved in isothermal treatments (1100 °C/min maximum) and in DSC tests (10, 20 and 40 °C/min) are lower than those of isothermal treatments in salt bath (18000 °C/min). What we want to show with the discussion contained in this paragraph is the sequence of the reversal mechanisms: it is initiated by the diffusion mechanism and then, at higher temperatures, the shear mechanism is activated.

In our isothermal treatments, lasting 1 hour, reversal begins around 400 °C, and the greatest decrease in Wt % martensite is for temperatures above 750 °C, Figure 2. For DSC tests, the A_s temperatures found are close to 450 °C, Table 4; but the maximum value of the reversal completion temperatures is 633 °C (A'_f, Table 4). We can say that as DSC heating rates are slow (10, 20 and 40 °C/min) with respect to heating rate in salt bath (18000 °C/min) the samples will have enough time for reversion to begin via diffusional mechanism, when they pass through the temperature range between T_0 and T_1. These temperatures were initially unknown for the steels studied here. As it was mentioned, in continuous heating conditions (as DSC tests) they are called A_s and A'_s respectively and depend on the heating rate. Then, when in each DSC test the corresponding $T_1 = A'_s$ temperature is exceeded, it will initiate the reversal via shear mechanism; but A'_s temperature could not be determined under the conditions of the tests carried out here. As already mentioned, the completion of the endothermic peak is associated with the ending temperature of the non-diffusional mechanism (A'_f). In KNUTSSON *et al.* [12] for a DSC test of a 61% cold worked AISI 301 steel, the authors observed that the reversion peak ended at ~600 °C, and this temperature was assigned to A'_f. This assignment for A'_f was supported by the fact that the amount of α'-martensite obtained was approximately the same for 1 hour isothermal treatments at temperatures of 600, 650, and 700 °C. Additionally, they observed that samples treated at 650 °C had 8 Wt % of α'-martensite, both for 6 min annealing and 1 hour annealing; but if the annealing times were increased to 90 hours, the amount decreased to 3 Wt %. Therefore, they concluded that for long times the reversal was completed in a diffusional way. For 700 °C and 800 °C isothermal HT, Figure 2, α'-martensite concentrations remain almost constant, this would indicate that A'_f temperature would be between 600 and 700 °C, which roughly coincides with the results presented in Table 4.

Therefore, for the samples studied here, reversion begins as diffusional at A_s temperature, then at a $A'_s < A'_f$ temperature the shear mechanism begins and overlaps the diffusional one. This overlap exists until the A'_f temperature, where the endothermic peaks of the DSC tests ends; and finally, the reversal would be completed by diffusion up to A_f temperature. A_f and A'_f could be determined in the DSC tests, Table 4; but A'_s and A_f could not be determined under the conditions of this work.

4.2. Transformation energies

In a DSC test at 20 °C/min heating rate, HAEßNER *et al.* [43], for a AISI 304 60% cold rolled steel and 12 Wt % of α'-martensite, the authors found that the energy of the endothermic peak, located between 470 and 550 °C, was 8 J/g. This value is very low compared to the values of 43 or 40 J/g obtained for AISI 304 steel heated to 20 °C/min, Table 5. A value of ~35 J/g for martensite formation energy in an Fe-18.5Cr-8.7Ni alloy was reported in TOMIMURA *et al.* [20] (when it is formed in a temperature range between 20 and –117 °C) (formation and reversion energies of martensite should be the same, but opposite in sign for a given material). This value is close to the results obtained for the 40 °C/min heating rate, between 37 and 43 J/g depending on the steel, Table 5; and the steel that comes closest to that energy value is AISI 304 (18.8Cr-9.2Ni).

In GRAHAM *et al.* [37] AISI 304 samples drawn at 0 °C with different degrees of deformation were studied. Using dilatometry, they determined that the reversion transformation was between 425 and 625 °C, when the samples were heated at 1 °C/min. They also determined the reversion energy by means of DSC tests at a heating rate of 50 °C/min and it turned out to be 33 J/g and 40 J/g for samples with 60 and 70 Wt % of α'-martensite, respectively. These energy values are like that obtained in our DSC tests for AISI 304 heated at 40 and 20 °C/min.

According to GHOSH *et al.* [13], for an AISI 304 steel, rolled at 0 °C and 25% reduction, DSC tests at a heating rate of 20 °C/min, showed two endothermic peaks, which indicated that the reversion reaction was divided into two stages, according to the authors. The first peak appears between 300 and 400 °C and has an energy of 36 J/g. The authors associate it with the dissolution of martensite and crystalline defects in small regions along the austenite/martensite interface. Then, between 400 and 450 °C, they record an interruption of the reversion due to the diffusion of iron and nickel through the austenite/martensite interface that seemed to stabilize the rest of the martensite. Finally, the second endothermic peak appears between 450 and 550 °C with an energy of 38 J/g. This second energy value is close to the values 43 and 40 J/g observed in the AISI 304 steel heated at 20 °C/min; both temperature ranges are also comparable, 430 and 580 °C, Table 5. It should be mentioned that only in GHOSH *et al.* [13] two endothermic peaks were found.

Figure 5 shows that as heating rates increase, the energy associated with reversion reaction decreases. Therefore, the total martensite reverted percentage at the end of the endothermic reaction (diffusionaly and non-diffusionaly) would be expected to be lower at higher heating rates, and that the remaining martensite has to be reversed only via diffusional mechanism at temperatures greater than that of the end of the endothermic reaction. This reduction in energy could be caused by the decrease in the reversal percentage corresponding to the diffusional mechanism, in the temperature range where the endothermic peak is located. Possibly at very high heating rates the energy would become constant, as would the start and end temperatures of the reversion peak reaction, which become constant for very high heating rates [15–17] where the reversion became completely non-diffusional. Thus, if the energy of the reversal were to become constant for very high heating rates, its value could also be associated with the energy corresponding to the shear reversal exclusively.

5. CONCLUSIONS

Through DSC tests it was estimated that, in continuous heating, most of the reversion occurs during the endothermic peaks: reversion begins via diffusional mechanism at temperature A_s (between 414 and 453 °C), and the end temperature of the endothermic peak would be the finishing temperature of the shear mechanism A'_f (between 557 and 633 °C). However, the endothermic peak completion temperature A'_f does not indicate that the reversal is complete, since the reversion is completed by means of diffusional mechanism when a temperature $A_f > A'_f$ is reached. With the tests carried out, it was not possible to determine the reversal start temperature due to shear mechanism cutting A'_s, but based on the literature it is estimated that this temperature falls between A_s and A'_f. The latter indicates that between A_s and A'_f and the two reversal mechanisms overlap. In addition, under the conditions of the tests of this work, the ending temperature of the diffusion reversion mechanism A_f could not be determined either.

For 1 hour isothermal treatments the reversion begins at temperatures higher than 400 °C and the greatest amount of martensite reverts between 450 ºC and 700 ºC. In AISI 304 and 347 steels, a small additional amount of martensite was formed in the isothermal HT carried out at 400 °C. This phenomenon is reported in the bibliography and occurs at temperatures prior to and close to the temperature of the start of the reversion.

The energy per unit mass of α' for the strain-induced reverse transformation was determined to be in the range 37-63 J/g. For all the steels studied, it was observed that this energy per unit mass decreases as the heating rate increases.

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