Technological application of the martensitic transformation of some austenitic stainless steels

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The final heat treatment of austenitic stainless steels of types X 5 CrNi 18 9 (1.4301) and X 2 CrNi 18 10 (1.4306) normally is annealing at 1050°C and subsequent water quenching. The resulting structure is of a metastable fcc-type. Plastic deformation, especially at low temperature, causes martensitic transformation of these metastable structure.

The transformation is accompanied by a substantial flow stress increase. This strengthening mechanism should be used in practice, e.g. for saving weight [1,2].

The deformed structure consists of tetragonal α' -martensite, austenite and hcp ϵ -martensite. Whereas α' -martensite increases continuously with deformation, the content of ϵ -martensite reaches a maximum value at about 5% plastic strain at 77 K. The hcp phase is only detectable by means of x-ray analysis whilst α' -martensite can be determined quantitatively by saturation magnetisation measurement.

The flow stress increase in low temperature deformation of metastable austenitic stainless steels is based on normal work-hardening by dislocation accumulation, in addition to a distinct amount of work-hardening due to martensitic transformation. Analysis of the work-hardening behavior in the range of stable deformation ($T > M_D$) can be used to predict the amount of normal work-hardening when deformation is performed in the instable temperature regime.

Figure 1 shows the normalized work-hardening coefficient (θ) vs. the normalized flow stress (σ) for the grade 304 (1.4301) in the temperature range from 293 K to 423 K.

Within this range deformation occurs nearly without martensitic transformation. The saturation stresses σ_s in the instable regime can be evaluated by extrapolating the stable values to lower temperatures.

On the basis of figure 1 the corresponding flow curves can then be predicted [3].

Separation of the flow stress contributions according to the procedure described above enables the possible savings in weight to be predicted when using cryogenically stretched instable austenitic steels in comparison with stable grades deformed under the same conditions.

Fig.1: Normalized work-hardening coefficient vs. normalized flow stress for different temperatures of stainless steel grade 304

Work hardening phenomenon of 18-8 CrNi-stainless steels

Standard tensile tests have been performed in the temperature range from 473 K down to 77 K in order to investigate work-hardening behavior of instable austenitic stainless steels. The slope of the flow curve $\theta = \partial \sigma / \partial \phi$ has been calculated and provides a powerful means for detecting structural changes during deformation. Figure 2 illustrates the situation:

Normalization of the axes with respect to the shear modulus $G(T)$ eliminates trivial temperature effects on work-hardening behavior; the range of stable austenitic deformation work-hardening is linearly related to the corresponding flow stress σ ; a loss of structural stability with decreasing test temperature may eventually cause slight deviations from linearity. This is especially true in the case of the room temperature work hardening curve. It is well known that severe deformation of type 304 stainless steel can cause martensitic transformation at and above room temperature. The linear dependence of the work-hardening coefficient upon the flow stress

$$\theta = \frac{\partial \sigma}{\partial \phi} = \frac{\theta_0 \sigma_s}{\sigma_s - \sigma_0} (1 - \sigma / \sigma_s) = \frac{\sigma_s}{\phi_c} (1 - \sigma / \sigma_s)$$

yields a simple exponential flow law

$$\sigma = \sigma_s + (\sigma_0 - \sigma_s) e^{-(\phi - \phi_0) / \phi_c}$$

the so-called Voce-equation. At low stresses all curves deviate from linearity. The starting point for linear behavior is indicated by the point P in figure 2 allowing the values for σ_0 to be read out of the diagram. Further constants of the Voce-equation can also be deferred from figure 2. The saturation stress σ_s can be determined by extrapolating the straight lines to zero work-hardening. The inverse of the slopes of the straight lines are equal to ϕ_0 - the so-called relaxation strain, the value of ϕ_0 can simply be read out of the flow curve [4,5/.

Fig. 2: Normalized work-hardening coefficient vs. normalized flow stress for different temperatures of stainless steel grade 304L

Work-hardening at 77 K is totally different and no longer linear with stress. At small stresses a minimum work-hardening rate is reached, which in fact can be smaller than the rate of work-hardening at the same stress level at room temperature (see fig. 2). In this initial stage the mechanical stability of deformation is small. The distance between the work-hardening curves and the Considère straight line may serve as a measure of the mechanical stability of a specimen deformed in tensile test; nevertheless, due to the structural instability, i.e. due to the martensitic transformation the work-hardening rate is greatly enhanced and the mechanical stability increases with deformation up to a maximum value. This effect also leads to sufficiently high value of uniform elongation.

Because of their comparatively low proof stress 18-8 CrNi stainless steels have been excluded from more extensive technological applications when there is a requirement for high strength. Pre-deformation at low temperature can also be used to enhance the proof stress of these steel grades. Cryogenically stretching of

austenitic pressure vessels can be referred to as a practical utilization of the special strengthening mechanism by martensitic transformation.

To check the efficiency of cyro-forming it would be necessary to assess the flow curve for deformation of a stable austenitic nature - even at 77 K. In other words, checking for the amount of normal work-hardening a metastable austenitic steel would undergo when deformed in tensile test at 77 K. Because all curves representing stable work-hardening intersect through point P in figure 2, one point of this curve is already known. To construct the whole flow curve it is also necessary to know the saturation stress. Determination of the saturation stress at 77 K can best be performed by an activation analysis of the already known saturation stresses. Figure 3 shows the results of an activation analysis of the saturation stresses obtained in the range of stable austenitic deformation.

The logarithmic values of the saturation stress normalized to the shear modulus decrease linearly with thermal energy. Saturation stresses in the instable regime can be evaluated by extrapolating the stable values to lower temperature (thermal energy). The corresponding flow curve can then be predicted utilizing figure 2.

Fig. 3: Normalized saturation stress vs. thermal energy for 18-8 CrNi-stainless steel grades 304 and 304 L

Fig. 4: Flow curves of the 18-8 stainless steel grade 304 L

1) room temperature flow curve; 2) flow curve at 77 K, stable austenitic material behavior; 3) flow curve at 77 K, real (instable) material behavior

Figure 4 shows the true stress strain curves of the steel grade 304L at 77 K for instable and stable austenitic behavior.

The room temperature flow curve is also included in figure 4. Austenitic stainless steels of types 304 and 304L do not reveal 0.2%-proof stresses much in excess of 200 MPa; nevertheless, austenitic steels as a consequence of their low stacking fault energy possess high work-hardening capacity even at higher temperatures. Cold-stretching, i.e. predeformation at ambient temperature, can thus be utilized to increase the proof stress. Equal amounts of predeformation at 77 K lead to considerable higher values only if martensitic transformation takes place. In the case of stable austenitic material behavior the effect will not be much greater than the one obtainable by room temperature deformation because the temperature dependency of the flow stress must be taken into consideration. Accordingly, the room temperature proof stress after cryo-forming of instable austenitic stainless steels is of important practical interest.

Technological application

In laboratory simulation of cryo-forming operations standard tensile specimens have been deformed at liquid nitrogen temperature with different amounts of total elongation. In the cryo-forming process the room temperature 0.2%-proof stress was determined and plotted against the flow stress value at each degree of predeformation. Figure 5 illustrates the results of laboratory cryo-forming.

Fig. 5: Effect of stress at degree of predeformation at liquid nitrogen temperature and room temperature

Due to the above mentioned temperature dependend proof stress of instable austenitic steels, the 0.2%-proof stress values do not exactly equal the flow stress values as predeformation is performed at ambient temperature in order to increase strength. It is obvious from investigation of figure 5 that the proof stress of instable austenitic steel grades 304 and 304L can be raised by cryo-forming to yield five times the initial value. The 0.2%-proof stress value indicated in figure 5 can be referred to as a minimum strength for pressure vessel application of steels. Should austenitic steel grade 304 meet this requirement, a minimum flow stress during cryo-forming operation of 900 MPa would be necessary. In accordance to the flow curve of grade 304 a plastic strain of 12% will then be reached. In principle, severe cold stretching can also be performed to raise proof stress up to 750 MPa. The associated strain would be much in excess of 20% thus inadmissible shape deformation may occur. Cryo-forming in comparison with cold-stretching yields higher proof stresses and associated strains are much lower when comparable strength values are aimed for. In comparison with other steels, e.g. quenched and tempered steels, cryo-formed instable stainless steels have better ducti-

lity. Table 1 summarizes some basic mechanical properties of a widely used heat-treated steel in comparison with those of the instable austenitic steel grade 304L.

	quenched and tempered steel 34 CrMo 4	cryo stretched austenite 1.4306 (grade 304L)
yield point R_p (N/mm ²)	> 755	> 755
tensile strength R_m (N/mm ²)	900	1050
elongation at fracture A_5 (%)	16	22
notch toughness a_K (J/cm ²) at -20°C	53	120

Tab. 1: Mechanical properties of a quenched and tempered steel and a cryo-formed instable stainless steel

Total elongation as well as absorbed energy is higher in notched bar impact bend test.

Savings in weight with structural components are due to reduced wall thicknesses when using cryo-formed instable austenitic steels in comparison with other stable austenitic or ferritic-austenitic steels. Figure 6 shows the weight of cylindrical pressure vessels used for storage of industrial gases versus volume content.

Fig. 6: Cylindrical pressure vessel weight vs. volume content

It is obvious from figure 6 that a stable austenitic steel (1.4429, grade 316LM) with some additional alloying (i.e. nitrogen, molybdenum) for raising proof stress to 310 MPa has about up to two or three times the weight of a cryo-formed cylindrical pressure vessel of grade 304L steel.

Figure 7 is a picture of a cylindrical pressure vessel used for the storage of industrial gas before (figure 7a) and after (figure 7b) cryo-forming. The shape deformation associated with the cryo-forming process is comparatively small.

Cryo-forming of instable austenitic stainless steels is not only attractive in a scientific sense but also in a financial sense as some of the alloy elements are much too expensive in today's market to be wasted.

Fig. 7: Cylindrical pressure vessel
a) undeformed, b) after cryo-forming

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