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A Mössbauer Spectrometry Study of the Mechanical Transformation of Precipitated Austenite in 6Ni Steel

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Abstract

A previous study suggested that precipitated austenite in "QLT" 6Ni steel is sufficiently stable to avoid transforming to martensite in the path of a propagating crack. Impact specimens of "QLT" 6Ni steel with differing geometries were broken at 77 K and 290 K. The depth of transformation of the austenite below the fracture surfaces was measured by backscatter electron Mössbauer spectrometry. The depth of transformation correlated with the impact energy and depth of the plastic zone, but was mostly independent of temperature. It is concluded that the martensitic transformation of precipitated austenite occurs in the plastic deformation ahead of the crack, and in ductile fracture the precipitated austenite will not remain to interfere directly with crack propagation.

Introduction

An intercritical tempering is standard commercial practice in the preparation of 6Ni and 9Ni steels for cryogenic service. The ductile-to-brittle-transition-temperature, T_b , of these steels can be reduced over 100°C by this heat treatment. It is well-known that the intercritical tempering introduces a few percent of precipitated austenite into the lath martensitic microstructure [1-4]. This austenite forms as slightly elongated regions of submicron dimensions situated between the martensite laths and along prior austenite grain boundaries. It is also known that the mere presence of austenite is not sufficient to ensure the suppression of T_b ; the austenite must possess reasonable stability against the martensitic transformation if good cryogenic toughness is to be realized [1,2,5]. Good cryogenic fracture toughness requires that the austenite not only be stable upon exposure to cryogenic temperatures, but also that the austenite be at least somewhat stable during mechanical deformation at cryogenic temperatures. The degree of mechanical stability required for good toughness is not fully understood.

A knowledge of the factors that influence the martensitic transformation of precipitated austenite is helpful in understanding how the austenite affects fracture toughness. Many explanations of how precipitated austenite affects fracture toughness involve considerations of when the austenite transforms during the fracture process [1-6]. For example, some early explanations proposed that the austenite was sufficiently stable so that it would directly interfere with crack propagation. These explanations were dispelled for 9Ni steel by recent Mossbauer spectrometry studies of fracture surfaces [7,8]. These studies showed that no austenite remained at the fracture surface, so the crack could not be blunted by the ductile austenite phase. In the case of 6Ni steel, however, austenite particles were observed in extremely close proximity to fracture surfaces of impact specimens of an unusual design. In these careful transmission electron microscopy (TEM) observations by Haga [3], iron was electroplated onto fracture surfaces of "constrained-fatigue-notched" (CFN) impact specimens shown in fig. 1. Foil specimens for TEM were prepared by slicing the electroplated specimens perpendicularly to the fracture surface so that the microstructure just below the fracture surface could be examined. In "QLT" treated 6Ni steel with rather stable precipitated austenite, Haga reported that the transformation of austenite occurred no further than 10 μm from the fracture surface. This observation suggested that in "QLT" 6Ni steel the austenite may directly interfere with crack propagation. The present study was motivated by this apparent conflict between the fracture surface studies of 9Ni steel and Haga's study of 6Ni steel.

Experimental Methods

Commercial 6Ni steel plate with the proprietary "QLT" heat treatment was kindly supplied by the Nippon Steel Company. The composition of this material was (in wt.%): 5.75 Ni, 0.93 Mn, 0.5 Mo, 0.19 Si, 0.16 Cr, 0.06 C, 0.06 P, 0.05 S with a balance of Fe. Impact specimens were prepared directly from this as-received plate. Both CFN specimens and standard ASTM Charpy V-notch specimens were prepared, and three specimens of each type were broken at both 77 K and at 290 K. Surfaces perpendicular to the fracture surface were prepared for visual and optical metallographic examination. With the discoloration produced by a Nital etchant, the depth of plastic deformation below the center of a fracture surface could be measured approximately.

The large plastic deformations and variations in crystallographic texture near fracture surfaces led us to choose Mössbauer spectrometry instead of x-ray diffractometry for measuring the amounts of austenite near fracture surfaces. ^{57}Fe Mössbauer spectra were obtained with a Ranger Scientific SD-300 detector that was modified to have a reduced active volume appropriate for the dimensions of the fracture surfaces. A mixture of 95 % He + 5 % CH_4 flowed through the detector so that backscatter electrons originating within a few hundred angstroms of the specimen surface were counted. Shear lips and the fatigue precrack were

masked with tantalum sheet so that only the centers of the fracture surfaces were analyzed. After amplification and discrimination, the detector pulses were counted with a microcomputer system [9] that also synchronized the motion of the Austin Science S-600 Doppler drive. A ^{57}Co in Pd radiation source was used for all spectra, and both source and specimen were at room temperature.

Depth profiling of the austenite content below the fracture surface was performed by chemically polishing the fracture surfaces in fresh solutions of 2 % HF, 29 % H_2O_2 , and 69 % H_2O . All four types of specimens in a set for comparison (standard Charpies broken at 77 K and 290 K, and CFN specimens broken at 77 K and 290 K) were polished simultaneously in the same solution. Weight losses of the specimens and optical microscopic examination were used to determine the depth of polishing. Nevertheless, it is still possible that our reported depths below the fracture surface have systematic errors of up to 50 %; a fracture surface does not polish evenly. As a check against the transformation of austenite during surface preparation [10], austenite contents were also measured by backscatter γ -ray Mössbauer spectrometry and by x-ray diffractometry in undeformed regions of bulk material. Good agreement (within 1 - 2 %) was found between the bulk amounts of austenite determined by the three techniques.

Results and Discussion

Three phases were identified from Mössbauer spectra of 6Ni steel. The ferromagnetic martensite phase displayed its characteristic spectrum of six peaks that were slightly broadened due to effects of solute elements. The relative intensities of the six peaks were approximately 3.0 : 2.6 : 1.0 : 1.0 : 2.6 : 3.0, indicating a slight tendency of the magnetization to lie within the plane of the specimen surface. The isomer shift of the martensite spectrum was +0.03 mm/sec with respect to pure Fe, and the average hyperfine magnetic field was approximately 336 kG. The one peak from the austenite phase was centered about a velocity of -0.06 mm/sec with respect to pure Fe. The full-width-at-half-maximum (FWHM) of the austenite peak was 0.38 mm/sec. The linewidth of our spectrometer was 0.25 mm/sec for pure Fe. The excess broadening of the austenite peak suggests a rich concentration of solute elements in the austenite, but the systematics of this chemical broadening were not explored. A discoloration was sometimes observed on the surfaces of specimens after polishing. This discoloration corresponded to a doublet peak with an isomer shift of +0.39 mm/sec with respect to pure Fe and a splitting of 0.62 mm/sec. This corrosion product was tentatively identified as $\beta\text{-FeOOH}$ on the basis of these spectral parameters [11].

The corrosion product interfered with austenite content measurements because one peak of its doublet was nearly coincident with the austenite peak. The other peak of the doublet was nearly coincident with the martensite peak at +0.59 mm/sec.

Since both peaks of the doublet have the same intensity, and since the two martensite $\pm 1/2 \rightarrow \mp 1/2$ peaks also have the same intensity, the austenite peak could be separated from the peak due to the corrosion product by a digital stripping procedure. In this procedure two Lorentzian functions appropriate to the martensite peaks were stripped from the spectrum so that the martensite peak at -1.1 mm/sec was completely removed. Examples of this procedure are shown in figs 2 and 3. In fig 2 it is apparent that only a doublet peak due to the corrosion product remains after stripping. Without stripping, the central bump in the spectrum might suggest the presence of 2 % austenite. After stripping the martensite peaks from the spectrum of fig 3, the austenite peak is clearly revealed. A corrosion product peak is also evident on the left tail of the austenite peak. The doublet could then be removed by stripping two Lorentzian curves characteristic of the doublet until the left peak of the doublet disappeared, and the remaining intensity should be entirely due to the austenite. When the area of the austenite peak, I_γ , was determined by numerical integration, it was compared to the area of a stripped $\pm 1/2 \rightarrow \mp 1/2$ martensite peak, I_α . The austenite volume fraction was then estimated as:

$$\% \text{ Austenite} = \frac{I_\gamma}{I_\alpha} \cdot \frac{100 \%}{[2 \cdot (3 + 2.6 + 1) + I_\gamma/I_\alpha]} \quad 1)$$

No correction was made for the different concentrations of Fe in the austenite and the martensite, but this correction is the same constant factor for all data. The presence of 10.5 % austenite is determined from fig 3 with the use of eqn 1.

Depth profiles of the amount of austenite below the fracture surfaces are shown in fig 4. No austenite (less than 1 %) was ever observed on the fracture surface of any specimen. Although no austenite particles were completely mechanically stable, they were all thermally stable with respect to an immersion in liquid nitrogen. As seen in fig 4, none of the austenite in the 77 K specimen transformed in those regions well-removed from the fracture surface. The austenite profiles below the fracture surfaces all have basically the same shape, but these profiles are shifted to increased depths in the order: 77 K CFN, 290 K CFN, 77 K Charpy, 290 K Charpy. This ordering of specimens is the same as their ordering in impact energy, which largely reflects the amount of plastic deformation during fracture. We use these data to compare the relative effects of temperature and plastic deformation on the transformation of austenite.

We define the transformation depth as the depth at which half of the precipitated austenite has transformed. Fig 5 shows the transformation depth as a function of impact energy. The consistent behavior of the five points in fig 5 is impressive. It is apparent that temperature does not play the major role in causing the transformation of austenite in 6Ni "QLT" steel. Although

there is no thermal transformation of the austenite in the absence of plastic strains, it might be expected that when the transformation was strain-induced, more transformation of austenite could be promoted at low temperatures. Such a thermo-mechanical effect on the transformation may exist, but it is largely buried within the monotonic behavior of the data of fig 5. Note that the datum from Haga [3] for his "QLT" CFN specimen broken at 77 K is also consistent with this trend. (The low impact energy of his CFN specimen is probably due to his high austenitizing temperature.)

The data of fig 5 suggest that the transformation depth is mostly a function of the plastic deformation during fracture. Optical microscopy showed that the depth of the plastic zone was 2 mm for the 290 K Charpy specimen, somewhat more than 1 mm for the 77 K Charpy specimen, and less than 1 mm for the two CFN specimens. Within a significant experimental uncertainty, the transformation of austenite begins at the maximum depth of the plastic zone. With greater certainty we can say that the transformation depth as we have defined it lies within the plastic zone. Furthermore, the transformation depth scales with the depth of the plastic zone. Given the same yield strength, the

* However, the yield strength at 290 K is 20 % lower than at 77 K [12]. This suggests a deeper plastic zone for a given impact energy at 290 K. Perhaps a reduced thermal driving force for the transformation at 290 K partially compensates for the otherwise greater transformation depth.

plastic zone should approximately scale with the square of the impact energy. This is consistent with the parabolic curvature of the data in fig 5, but such detailed agreement may be fortuitous.

Conclusions

The transformation of precipitated austenite in "QLT" 6Ni steel is primarily a function of plastic deformation, and not temperature. The depth of transformation below a fracture surface will be greater in those specimens that are tougher and exhibit more plastic deformation. In particular, the close proximity of the austenite particles to the fracture surfaces of Haga's specimens is due to the very brittle mode of fracture in his material. We conclude that when good fracture toughness is exhibited by 6Ni "QLT" steel, the austenite particles have transformed before they can interact directly with a propagating crack.

Acknowledgments

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Fig. 1 Constrained-fatigue-notched specimen geometry.
After Haga [3].

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Fig. 2 Mössbauer spectrum from 77 K Charpy specimen polished 0.01 cm showing no austenite after stripping.

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Fig. 3 Mössbauer spectrum from material well-removed from the fracture surface of 77 K Charpy specimen.

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Fig. 4 Depth profiles of austenite contents below fracture surfaces.

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Fig. 5 Transformation depth versus impact energy.

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