

# Mechanical Stability of Retained Austenite in Tempered 9Ni Steel

C. K. SYN, B. FULTZ, AND J. W. MORRIS, Jr.

The behavior of the thermally stable austenite in the ductile fracture surface layer of a grain-refined and tempered 9Ni steel broken at 77 K was studied through use of Mössbauer spectroscopy and transmission electron microscopy. Thin foils revealing the microstructural profile of the fracture surface layer were prepared by electroplating a thick pure iron layer on the fresh fracture surface, then thinning a profile sample through a combination of conventional twin-jet electropolishing and ion milling techniques. The results of both Mössbauer spectroscopy and TEM studies showed that the thermally stable austenite transforms to a dislocated martensite in the deformed zone adjacent to the ductile fracture surface. This result suggests that transformation of the retained austenite present in tempered 9Ni steel is compatible with low temperature toughness, at least when the transformation product is a ductile martensite.

PROPERLY tempered Fe-(5-9)Ni<sup>1-3</sup> steels for cryogenic use contain a small admixture of retained austenite (5 to 10 pct by volume) which is believed to contribute to good low temperature toughness. The retained austenite is precipitated as small elongated particles along martensite lath boundaries and prior austenite grain boundaries, as illustrated in Fig. 1. If introduced by tempering in the lower portion of the two-phase ( $\alpha + \gamma$ ) region of the equilibrium phase diagram, at temperatures in the range 500 to 600°C, the austenite is thermally stable and does not transform to martensite when cooled to liquid nitrogen temperature (77 K).

While it is widely accepted that precipitated and retained austenite has a beneficial effect on cryogenic mechanical properties the source of the effect is not well understood. Plausible explanations have been based both on the chemical properties of the austenite,<sup>3,4</sup> in that it may "getter" potentially embrittling species, and on its low temperature mechanical properties<sup>1-5</sup> in that austenite is a relatively ductile phase which may enhance local ductility or blunt propagating fractures. Either explanation is, however, complicated by the question of the mechanical stability of the austenite; while the austenite is thermally stable it may nonetheless undergo catastrophic transformation to martensite in the intense deformation field near the tip of a propagating crack.

Research in recent years has particularly emphasized the importance of the mechanical stability of retained austenite to the low temperature toughness of Fe-Ni cryogenic steels. It was noted some time ago that the beneficial effect of retained austenite formed during tempering decreases dramatically as the tempering temperature is raised above ~575°C, a result which has been attributed<sup>6</sup> to a decreasing mechanical stability of the austenite due to

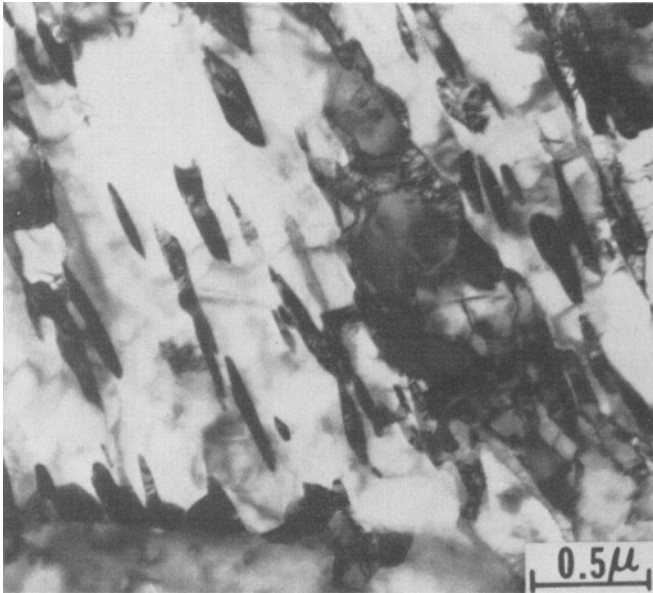
lower nickel content at higher temperatures of formation. More direct evidence for a causal connection between austenite instability and low temperature embrittlement was obtained by Kron *et al*<sup>7</sup> who conducted an extensive fractographic analysis of 9Ni steel samples fractured below the ductile-to-brittle transition temperature. They observed an apparent promotion of brittle fracture by cleaved particles in the fracture surface which appeared to be transformed austenite. The evidence led Nagashima *et al*<sup>1</sup> to list mechanical stability of retained austenite as a major metallurgical requirement in their successful development of a 6Ni cryogenic steel. Their reasoning appeared to be confirmed by the corollary metallographic studies of Haga<sup>8</sup> who artificially introduced brittle fracture into a 6Ni steel sample at 77 K and successfully prepared a profile TEM fractographic specimen of the broken surface. His transmission electron microscopic studies show the retention of austenite to within a few microns of the fracture surface. Apparent austenite transformation to a twinned martensite is occasionally observed, suggesting that the specimen would have been brittle had more extensive transformation taken place.

The conclusion that retained austenite must be stable to impart low temperature toughness is, however, seriously called into question by results obtained during the last two years. Using Mössbauer spectroscopy to perform quantitative analysis of the residual phases present in fracture surfaces both Kim and Schwartz<sup>9</sup> and Fultz<sup>10</sup> found essentially complete transformation of retained austenite near the ductile fracture surface of 9Ni steel specimens broken above the ductile-brittle transition temperature. The Mössbauer evidence is not definitive, since it cannot distinguish a transformation which occurred during fracture from one which happened after the fracture was complete. However, this evidence does suggest both a counterexample to the conclusion that austenite must be mechanically stable in cryogenic steels and a puzzle, since it is not clear how the fracture could remain ductile in the presence of the brittle transformation products found by Kron *et al*<sup>7</sup> and by Haga.<sup>8</sup>

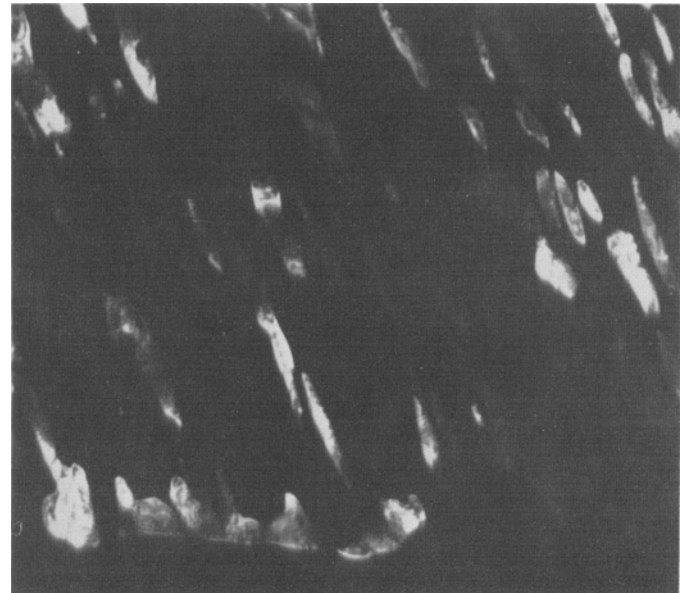
To clarify the issues raised by the Mössbauer evi-

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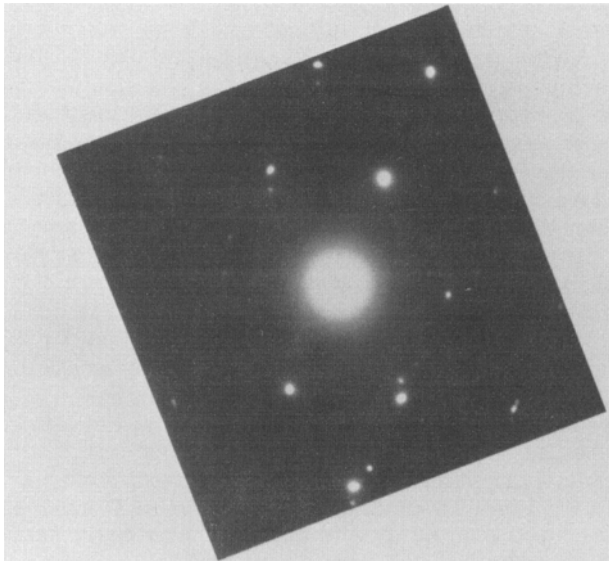
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(a)



(b)



(c)

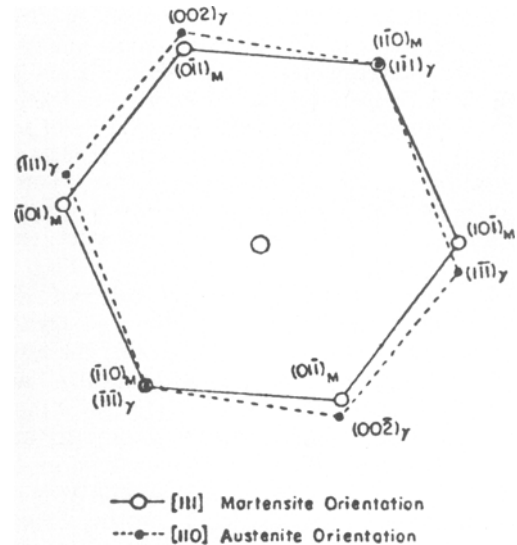


Fig. 1—Transmission electron micrographs of retaining austenite in grain refined and tempered 9Ni steel. (a) bright field, (b) dark field taken from  $(00\bar{2})\gamma$  diffraction spot in (c).

dence cited above we undertook a transmission electron microscopic study of the structure near the ductile fracture surface of a tempered 9Ni steel specimen broken at liquid nitrogen temperature. The direct observation of the structure immediately adjacent to the fracture surface required the preparation of profile fractographic specimens for TEM, *i.e.*, foils containing the fracture surface which are sufficiently thin for transmission studies. To our best knowledge no such studies have previously been made on a ductile fracture surface in a high strength steel; hence a major part of this work involved the development of sample preparation techniques.

#### EXPERIMENTAL

A 9Ni steel plate of 30 mm thickness was supplied by the Nippon Steel Corporation. Its chemical com-

position is given in Table I. Compact tension fracture toughness specimens were cut out of the plate. To insure that these specimens would fail in a ductile manner at 77 K the as-received microstructure was erased by annealing at 900°C for two h, and the specimens were given the grain refinement treatment shown in Fig. 2. After grain refinement the specimens were tempered at 575°C for one h and water quenched. The final microstructure of the specimens is illustrated in Fig. 1. Previous work<sup>11</sup> has shown that this grain refinement plus tempering treatment

Table I. Chemical Composition, in Wt Pct

C	Si	Mn	P	S	Ni	Fe
0.06	0.20	0.56	0.004	0.004	9.25	Balance

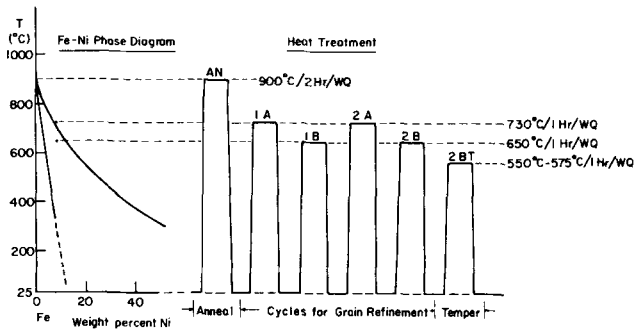


Fig. 2—Thermal cycling and temper procedure for grain refinement in 9Ni steel.

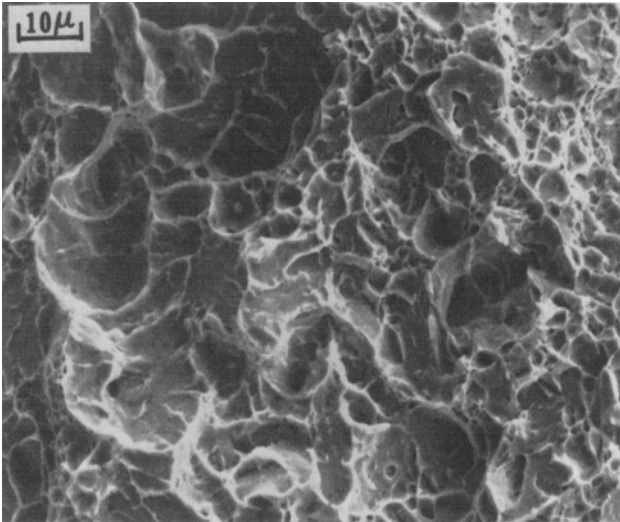


Fig. 3—Scanning electron microscopic (SEM) fractograph. Tempered (575°C/1 h/water quench) after grain-refinement and fractured in the compact tension test at 77 K.  $K_{IC}$  estimated to be 300 ksi  $\sqrt{\text{in.}}$  (330 MPa  $\sqrt{\text{m}}$ ).

suffices to reduce the ductile-to-brittle transition temperature of 9Ni steel to below 6 K. Fracture toughness tests were conducted on these specimens in liquid nitrogen (77 K) with the result that the specimens failed in a ductile manner (Fig. 3) with a fracture toughness ( $K_{IC}$ ) estimated to exceed 300 ksi  $\sqrt{\text{in.}}$  (330 MPa  $\sqrt{\text{m}}$ ), in agreement with earlier results.

One of the two matching parts of a specimen fractured at 77 K was used for Mössbauer spectroscopy. The fracture surface of the other piece was electroplated with pure iron to a thickness of more than 2 mm using the Fischer-Langbein type solution.<sup>12</sup> The plated piece was sliced along the direction of the fracture crack propagation and perpendicular to the fracture surface. These slices, ~500  $\mu\text{m}$  thick, were chemically and mechanically thinned to a thickness of ~40  $\mu\text{m}$ . Discs of 3 mm diam were then spark cut from the slices in such a way that the boundary lines between the plated iron layer and the fractured 9Ni steel lay approximately along a diam of the disc (Fig. 4).

The radius of the plastic zone in these fractured 9Ni samples was estimated to be 5 mm,\* an estimate

\*The radius of the plastic zone size ( $r_p$ ) was estimated from the formula for plain strain condition  $r_p = (K_{IC}/\sigma_y)^2/6\pi$  where  $K_{IC}$  is the fracture toughness and  $\sigma_y$  the yield strength (see Ref. 13). The  $K_{IC}$  value is given in the text. The yield strength of 9Ni steel measured at liquid nitrogen temperature is about 150 ksi (1034 MPa).

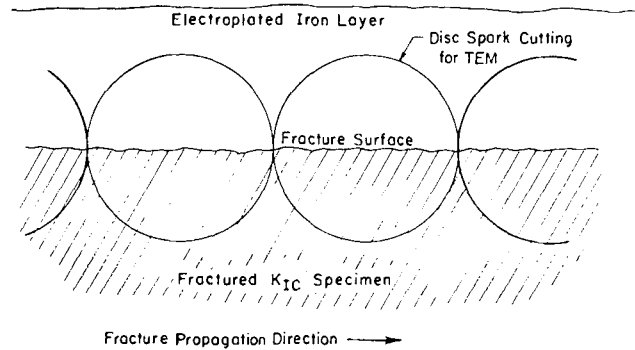


Fig. 4—Schematic diagram of disc preparation from the boundary area between the fractured 9Ni steel and the electroplated iron layer.

which is consistent with the observations of the fracture surface reported below. The 3 mm discs hence contained undeformed electroplated iron in intimate contact with severely deformed 9Ni steel of complex microstructure, posing a sample thinning problem of particular severity. TEM specimens were successfully prepared in a two-step process. First, each disc was electropolished using the familiar twin-jet method in chromium trioxide-glacial acetic acid solution (composition: 75 g  $\text{CrO}_3$  + 400 ml  $\text{CH}_3\text{COOH}$  + 21 ml distilled water) at ~40 to 45 V for two to three min until a small hole was formed at the center. The area around the hole was then further thinned by ion milling. The ion milling was performed with argon ion bombardment under the conditions: 6 KeV acceleration potential, 25  $\mu\text{A}$  ion current and 15 to 20 deg tilt angle. After ion milling the 9Ni steel side of the disc was found to be slightly etched. The area around the hole was, however, thinned sufficiently for observation in a high voltage microscope operated at 650 KeV, and was sufficiently uniform to permit detailed studies of the microstructure immediately adjacent to the fracture surface.

Mössbauer analysis was carried out with a spectrometer which contained an Austin Science Associates velocity drive synchronized to a Packard 400 multi-channel analyzer. The detector was of the Spijkerman type<sup>14</sup> operated for backscatter electron detection. Conversion electrons originating within ~0.1  $\mu\text{m}$  of the surface were counted. Distinct spectral lines were observed and the volume fraction of austenite was determined from the seven peak approximation.<sup>15</sup> By sequentially analyzing the fracture surface and the undeformed specimen surface well away from the fracture surface the comparative changes in the fracture surface could be directly determined. The fracture surface was electropolished for further analysis to determine the variation of austenite volume fraction with depth.

## RESULTS

### a) Mössbauer Spectroscopy

The results of the Mössbauer analysis are presented schematically in Fig. 5. The undeformed specimen surface shows a clear austenite peak corresponding to a retained austenite content of 8 pct by volume. This peak is absent in the spectrum obtained from the fracture surface suggesting an essentially complete transformation of the austenite over the region (to

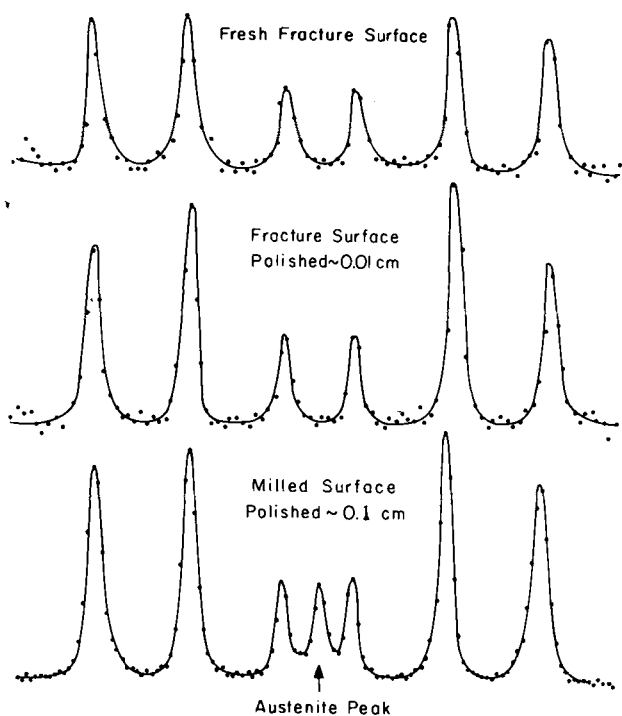


Fig. 5—Conversion electron Mössbauer spectra from the fracture surfaces. Solid curves were hand-drawn through datum points.

$\sim 0.1 \mu\text{m}$  below the fracture surface) from which the data is taken. The austenite peak was also absent from the spectrum taken from the fracture surface after electrolytic etching to a depth of  $\sim 1 \text{ mm}$ . This result suggests a general transformation to a significant depth within the plastic zone associated with the fracture, whose radius is estimated to be  $5 \text{ mm}$  for this particular case.

#### b) Transmission Electron Microscopy

The profile fractographic samples prepared for this study permitted examination of the region below the fracture surface to a depth of  $\sim 20 \mu\text{m}$  in a transmission electron microscope operated at  $650 \text{ KeV}$ . Typical bright field micrographs are shown in Figs. 6 and 7. The fracture surface is easily located by the abrupt change in microstructure between the electroplated iron layer (above) and the deformed 9Ni steel (below) and is marked with a dashed line and arrows respectively. The severe deformation of the alloy immediately below the fracture surface is visually apparent. Figure 7 includes a selected area diffraction pattern taken from the central region of the micrograph immediately below the fracture surface. The spread of the diffraction spots along each diffraction ring is indicative of the severe deformation of the subsurface material; as shown in Fig. 1 the selected area diffraction from the undeformed material yields a well-defined spot pattern. No extra spots attributable to retained austenite are present in the diffraction pattern.

A careful survey of the deformed region below the fracture surface to a depth of  $\sim 20 \mu\text{m}$  yielded no diffraction evidence for retained austenite, despite the

fact that features which morphologically resemble the retained austenite present in the undeformed alloy are common. Examples of austenitelike features are circled in Figs. 6 and 7; they are comparable to the retained austenite particles present in the dark field micrograph in Fig. 1. The TEM study hence supports the conclusion from Mössbauer analysis that there is complete transformation of the austenite near the fracture surface.

The TEM evidence argues, however, that the transformation of the austenite is in this case to a dislocated martensite rather than to a twinned martensite as suggested by earlier work.<sup>8</sup> In a careful structural survey of the subsurface region no example of internally twinned martensite was found. In particular, the martensite particles which were tentatively identified as transformed austenite on morphological grounds were dislocated rather than twinned. Examples include the circled regions in Fig. 6.

#### DISCUSSION

The evidence presented above appears to justify the conclusion that the retained austenite present in this grain-refined 9Ni steel specimen transformed to a highly dislocated martensite in the plastic zone associated with ductile fracture at  $77 \text{ K}$ . The only alternative explanations of the data which suggest themselves are that the fracture propagated through a region which was initially free of retained austenite or that the transformation to martensite occurred during relaxation of the free surface after fracture. Given



Fig. 6—Transmission electron micrograph and diffraction pattern of the fracture surface layer. The boundary between the electroplated iron layer (above) and fractured 9Ni steel (below) was marked by a dashed line. The circled areas show retained austenite-like particles.



Fig. 7—Another TEM picture of the fracture surface layer (the boundary indicated by arrows). The diffraction pattern was taken from the central region right below the boundary line. The circled area shows retained austenite-like particles.

the uniform distribution of retained austenite in the initial specimens, the depth of the zone denuded of austenite beneath the fracture surface, and the observation of significant austenite content near other free surfaces of the specimen, neither of these alternative explanations seems plausible.

Transformation of the retained austenite to a dislocated martensite is not inconsistent with good low temperature toughness, and would, in fact, be expected to favor ductile fracture. The austenite formed on tempering at 575°C is expected to be high in nickel relative to the base alloy; a nickel content near 20 at. pct is estimated from the equilibrium phase diagram. Moreover, the austenite forms submicron-sized particles in the lath boundaries of the parent martensite. The product of the strain induced transformation of this austenite, a high-nickel dislocated martensite of sub-micron size, should be even more ductile than the surrounding matrix and should not introduce preferential sites for cleavage fracture. On the contrary, the presence of this transformed austenite should inhibit brittle fracture in the plastic zone near the crack tip by preventing inter-lath fracture and interfering with the cooperative cleavage of adjacent laths. Moreover, by Le Chatelier's principle, the transformation strain associated with the martensitic transformation of the retained austenite will tend to relax the fracture stress, hence further promoting ductile failure.

It is not entirely clear how the previous results of Haga<sup>8</sup> and of Kron *et al.*<sup>7</sup> may be reconciled with the results presented here. Further investigations are in progress in this laboratory. However, it is almost

certainly relevant that both investigations considered the behavior of retained austenite during essentially brittle fracture. In Haga's case the presence of retained austenite near the fracture surface may simply reflect the narrow zone of deformation near the brittle fracture surface he obtained. The twinned martensite particles appearing in his micrograph may result from the difference in the composition of his alloy, from thermally-induced partial transformation of the austenite, from transformation near the free surface after fracture,<sup>16</sup> or from a change in the mode of austenite transformation due to the high rate of brittle crack propagation. The results of Kron *et al.*<sup>7</sup> are ambiguous since it has not been conclusively shown that the cleavage features they observed are due to the mechanically-induced transformation of austenite. If their interpretation of their data is correct their evidence indicates that the low temperature fracture behavior of 9Ni steel is sensitive to the mechanical properties (and hence to the microstructure) of the martensitic product of the strain-induced transformation of retained austenite, a result which is not inconsistent with the observations reported here.

## CONCLUSIONS

Both Mössbauer spectroscopy and direct transmission electron microscopic study show that the thermally-stable austenite introduced on tempering a grain-refined 9Ni steel at 575°C transforms to martensite in the deformed zone associated with ductile fracture at 77 K. The TEM evidence indicates that the transformation product is a sub-micron sized dislocated martensite which does not embrittle the alloy and may act to promote low temperature toughness. These results argue that it is not necessary that the austenite introduced on tempering ferritic Fe-Ni cryogenic steels be mechanically stable to promote low temperature toughness. A sufficient requirement is that the austenite transform to a ductile martensite during fracture.

A corollary result of this work is the demonstration that it is practical to make profile fractographic samples for transmission electron microscopic study of ductile fracture in steel. This technique should have wide application in cases where local microstructural effects are believed to be relevant to the fracture process.

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