JOURNAL OF MATERIALS SCIENCE 22 (1987) 3129–3138

Annealing of shear bands in metallic glasses

P. T. VIANCO, J. C. M. LI
Materials Science Program, Department of Mechanical Engineering, University of Rochester, Rochester, New York 14627, USA

Shear bands introduced into the as-quenched metallic glass alloy, Metglas^R 2826 ($Fe_{40}Ni_{40}P_{14}B_6$), were etched by immersion in a solution of $CuSO_4$ and HCl. Elimination of the etchability property through isothermal annealing had an apparent activation enthalpy of 250 kJ mol^{-1}, similar to that of stress relaxation. Direct microscopic observations indicated that the etching of shear bands may be a result of stress corrosion cracking. The electrochemical etchability of shear bands in the nickel-based alloy, BNi_2 ($Ni_{68.8}Cr_{6.6}Fe_{2.6}B_{14.1}Si_{7.9}$), polarized in a solution of perchloric acid and acetic acid at 12° C, could also be eliminated by thermal annealing. The loss of etchability had an apparent activation enthalpy of 580 kJ mol^{-1}, a value indicative of more complex atomic rearrangements taking place within the deformed material. Finally, shear bands introduced into the as-received BNi_2 material retained the ability to reverse shear after heat treatment at temperatures in the range of 192 to 375° C even if the electrolytic etchability was apparently diminished.

1. Introduction

Plastic deformation in metallic glasses has been categorized as either homogeneous or inhomogeneous. During homogeneous flow, all atomic sites are expected to contribute to the macroscopically observed dimensional changes. On the other hand, deformation is described as inhomogeneous when plastic flow is localized in particular regions of the ribbon termed shear bands. Shear bands are those areas of intense plasticity separating undeformed sections of material which have displaced relative to one another. Because shear bands are only about 10 to 20 nm thick [1], they are not readily observable on the sample surface. Rather, their presence is indicated through the surface step created by the relative shear displacement across the thin layer of deformed material (see Fig. 1).

In his work on Pd–Cu–Si amorphous alloys, Pampillo [2] discovered that he could electrolytically etch shear bands, the steps of which he had previously polished away, using a nitric acid–methanol solution at 0° C and a potential of 10 V. Chen *et al.* [3] were able to etch shear bands electrochemically in palladium-, platinum-, nickel-, and iron-based metallic glasses with an orthophosphoric acid–lactic acid solution and a 0.2 V potential. Therefore, as is similarly observed in the case of crystalline metal defects, the slip band was more chemically active than the surrounding undeformed material. After further experimentation, Pampillo also discovered that if the sample containing shear bands was thermally annealed (1 h at 325° C for his alloy), the electroetching property of the shear bands was lost. Assuming the deformed material to be a localized region of structural disorder relative to the bulk material, Pampillo reasoned that the loss of chemical activity was caused by an annealing-induced re-ordering within the shear band.

While working with the iron–nickel amorphous alloys, Metglas* 2826 ($Ni_{40}Fe_{40}P_{14}B_6$; subscripts denote atomic per cents) and 2826B ($Ni_{40}Fe_{29}P_{14}B_6Si_2$), it was determined that shear bands were also susceptible to chemical etching (that is, chemical attack without an applied potential). The best results were achieved on the 2826 alloy with a copper sulphate–hydrochloric acid solution while slip bands in the 2826B material were preferentially etched in a ferric chloride–hydrochloric acid–methyl alcohol solution. Moreover, it was also noted that the chemical etchability of shear bands could be eliminated by thermally annealing the deformed sample. In the first series of experiments to be reported in the present paper, the goal was to determine the annealing time and temperature parameters causing a loss of the chemical etchability of shear bands in the 2826 metallic glass alloy. Assuming that the recovery of the deformed structure can be represented by the following kinetic law:

$$\frac{dn}{dt} = -f(n)\,e^{-E/kT} \qquad (1)$$

where n is a parameter quantifying the etchability property; $f(n)$ is some function of n; E is the apparent activation enthalpy; and kT is the product of the Boltzmann constant and the absolute temperature, the analysis outlined by Parkins *et al.* [4] indicates that the apparent activation energy can be determined from the time–temperature combinations giving rise to a loss in etchability through the equation

$$\frac{d\ln(t)}{d(1/T)} = \frac{E}{k} \qquad (2)$$

---

*Registered trademark of the Allied Corporation.

0022–2461/87 $03.00 + .12

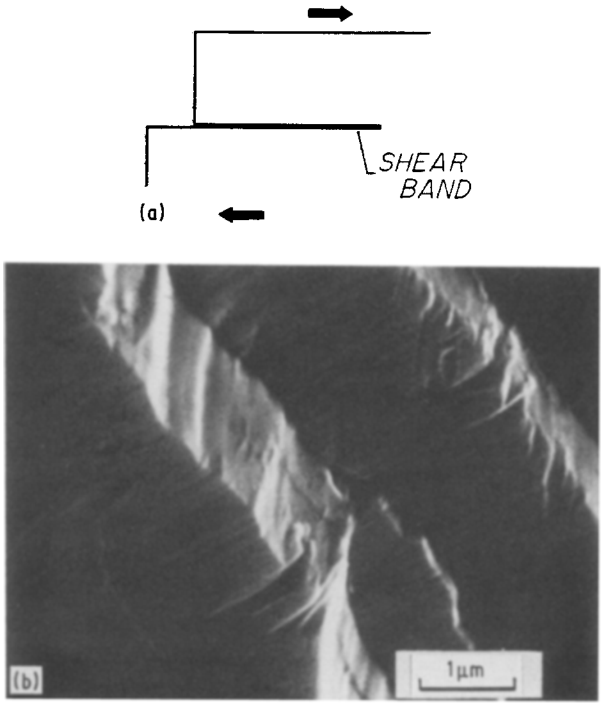

Figure 1 (a) Schematic diagram of a shear band. (b) Slip steps accompanying shear band formation in as-quenched Metglas 2826 amorphous alloy. (SEM.)

Then, by comparing the value of E with that of other processes documented in this or similar alloys, further insight into the structure of shear bands may be gained. To augment the present study of chemical attack of slip bands formed in metallic glasses, the same analysis was also performed on the electrolytic etchability of shear bands in a nickel-based metallic glass.

Finally, in a review of deformation behaviour of metallic glasses, Pampillo [5] described a reverse bending experiment. He bent a piece of $Pd_{83}Si_{17}$ amorphous alloy and, after carefully making note of the shear steps which had formed, he then bent the ribbon in reverse. Upon re-examining the same deformed region, he discovered that those slip bands formed in the initial deformation had also sheared in reverse. An example of this phenomenon is shown in Fig. 2 in which an as-received ribbon of Metglas 2826 was polished and subsequently bent to an angle of 71°, thereby causing the formation of the slip steps in (a) due to the tensile fibre stresses. The ribbon was then bent backwards to an angle of 151° and the same region as in (a) was rephotographed and is shown in (b). The reverse deformation was completely accommodated by the pre-existing shear bands; no new bands were apparently formed (to within the resolution of the micrographs). Deformation occurring preferentially at the pre-existing shear bands demonstrated an apparent softening of the deformed structure relative to the undeformed material [6]. As part of the investigation to be reported here, the reverse shearing property will be examined as to its persistence following a series of isothermal annealing treatments. This set of experiments will detail the more generalized results noted by Cao and Li [7].

2. Experimental procedures

2.1. Chemical etching of shear bands

The material used in the chemical etching experiments was Metglas 2826 ($Ni_{40}Fe_{40}P_{14}B_6$). Sample ribbons 50 mm long, 3.0 mm wide, and 0.043 mm thick were cut from the stock and one face polished with 600 grit silicon carbide paper to remove the large surface asperities. Each specimen was then lapped successively with 1.0 and 0.5 μm alumina suspensions. Shear bands were introduced into the ribbons by bending them between two flat plates. The degree of deformation was controlled by the minimum separation permitted between the two plates. A particular region of slip steps was then located and photographed with the optical microscope using the differential interference contrast (DIC) technique.

After the initial photographs had been taken, the samples were then thermally annealed in a quartz-tube vacuum furnace. Each sample was placed between two copper platens. One thermocouple probe was then inserted into the platens to record the sample temperature while a second probe provided the feedback signal to the temperature controller. The temperature stability was better than ±0.25° C. Upon completion of the annealing treatment, the samples were removed from the furnace and quenched in water.

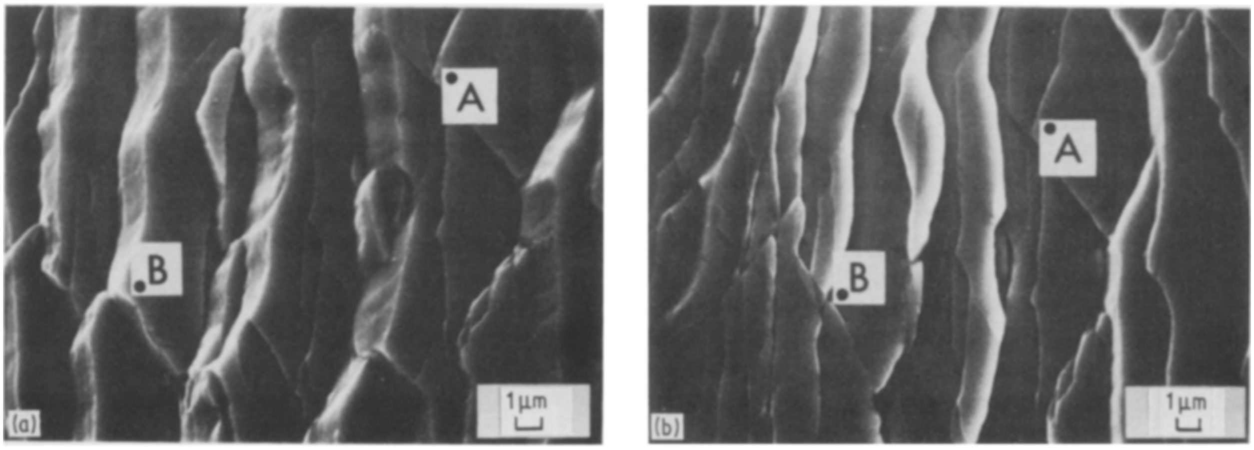

Figure 2 Reverse shear of shear bands in as-quenched Metglas 2826 alloy. (a) Slip steps produced by tensile fibre stresses (directed horizontally outwards) during forward bending. (b) The same region after "reverse" bending (compressive fibre stresses directed horizontally inwards). (SEM.)

Observation of the slip steps immediately after annealing indicated no recovery of the shear deformation to within the resolution limit of the scanning electron microscope (approximately 80 nm).

Next, the ribbons were polished with the 0.05 μm alumina slurry for approximately 3 min to remove the slip steps. Each sample was checked to make certain that no trace of prior deformation was present. This polishing procedure was performed after the heat treatment for two reasons: First of all, it was necessary to eliminate the oxide layer formed on the samples by air and water vapour which were trapped in the vacuum system as well as oxide caused by the quenching process so as to improve surface observation. Secondly, it was determined that the degree of surface susceptibility to chemical attack was a strong function of the annealing parameters (and the resulting character of the surface oxide). Therefore, to ensure that similar surface conditions would prevail for all of the samples when chemically etched, each was polished following the heat treatment.

Selection of the etchant was based upon compositions similar to those used on nickel-based crystalline alloys [8]. The solutions composed strictly of acid mixtures were ineffective. The addition of inorganic compounds (e.g. copper sulphate, ferric chloride, etc.) greatly enhanced the etchability of the bands. The etchant selected for this study contained 50 ml HCl, 10 g $CuSO_4$, and 5 ml H_2O. The sample was immersed in the room-temperature solution for 5 sec. After being rinsed in methyl alcohol and dried, the specimen was returned to the optical microscope; that region of deformation initially photographed was then located; and finally, photographs were taken of the etched (or unetched) slip bands.

2.2. Electrochemical etching of shear bands

For this series of experiments, the amorphous alloy MBF 20/20A ($Ni_{68.8}Cr_{6.6}Fe_{2.6}B_{14.1}Si_{7.9}$), also designated as BNi_2, was used due to a limited quantity of the other alloy. Ribbons 76 mm long, 3.2 mm wide, and 0.03 mm thick were taken from the stock. The same surface preparation and thermal annealing procedures as used on the 2826 alloy, were also employed in the electrolytic etchability study of the BNi_2 material.

The electrochemical etching process was carried out in a standard series cell. Those electrolytes normally recommended for nickel-based crystalline alloys [9] which are mixtures of perchloric and acetic acids, were found to etch shear bands successfully in the BNi_2 alloy. The optimum working solution was found to be 21% perchloric acid (60% concentration) and 79% acetic acid held at 12 to 14° C and constantly stirred. The cathode was type 304 stainless steel and the sample holder was constructed of polycarbonate. The current–voltage diagram for the given working conditions designated the electrolytic etching voltage at 2.1 V. The corresponding current density was 6.5 mA cm^{-2}. The etching period was 30 min, after which the sample was removed from the cell, rinsed in distilled water and alcohol and then allowed to dry. The position of those slip steps photographed prior to the heat treatment and electrochemical etching procedures, was located and rephotographed to evaluate the etchability of the shear bands.

Unfortunately, the corrosion resistance imparted by the high nickel content and chromium addition made it extremely difficult to etch shear bands chemically in this material. In those few cases in which the bands were revealed (through mainly solutions of hydrochloric, hydrofluoric and nitric acids), the surface was so badly attacked that their observation was extremely difficult.

2.3. Reverse shear band deformation

Samples with dimensions similar to those in the electrolytic etching study were used in this investigation. After the surface had been polished to a 0.05 μm alumina finish, shear bands were introduced into the ribbon by bending between two plates as described earlier. In this case, however, a greater degree of bending was utilized so that the resulting large distribution of step heights (and corresponding distribution of shear band lengths) would offer an evaluation of the effect of this property on the reverse deformation following annealing. The shear steps were photographed prior to annealing with the use of an ISI Super IIIA scanning electron microscope operated at 15 V.

The larger degree of bending precluded the samples from being annealed in the vacuum furnace because constraining them between the copper platens would cause further deformation (creep) under the high-temperature conditions. Without the platens, accurate determination of the sample temperature would not have been possible. Fortunately, because these alloys were abundant in nickel and chromium, they were extremely resistant to oxidation. Therefore, the samples were heated in air inside a resistance furnace. In fact, surface oxidation was first observed on those specimens annealed at temperatures in excess of 325° C and was not a problem for surface observation. Temperature control was maintained to within ± 1° C. Because of their small mass, the ribbons could be cooled to room temperature within 45 sec after being removed from the furnace.

Following the heat treatment, the samples were straightened by bending them in the reverse direction between the thumb and forefinger. The specimens were re-cleaned, placed into the scanning electron microscope at exactly the same orientation and operating conditions as in the initial pictures; and micrographs taken of the same slip steps, as observed before the annealing treatment.

3. Results

3.1. Chemical etchability of shear bands

An example of the chemical etchability of shear bands in the as-received 2826 alloy is shown in Fig. 3. The slip steps in (a) which identified the shear band locations, were polished away. The sample was then etched in the copper sulphate–hydrochloric acid solution for 5 sec. The etched shear bands appear in Fig. 3b. Close comparison of the two micrographs indicates that although the polishing process removed the slip steps from the ribbon, the shear bands themselves were not

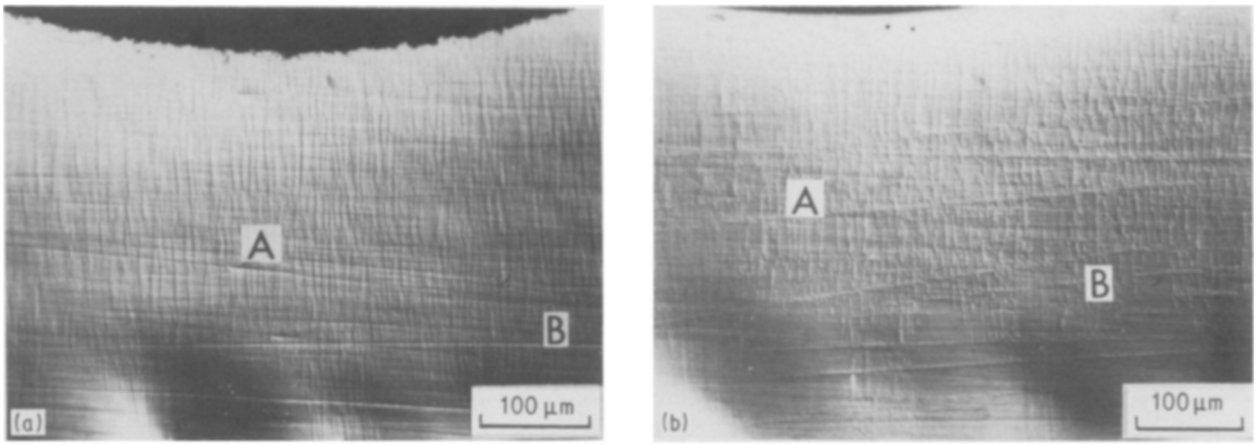

Figure 3 Chemical etching of shear bands in the as-quenched 2826 alloy. (a) Slip steps prior to etching. (b) Shear bands etched by immersion for 5 sec in a solution of 10 g $CuSO_4$–5 ml H_2O–50 ml HCl after a polishing treatment to remove the steps. (Optical-DIC.)

polished away as evinced by their presence in the latter picture. In addition to the attack specific to the shear bands, a black tarnish covered the entire surface of the ribbon exposed to the etchant. However, it did not interfere with surface observations.

The effect of thermal annealing on the chemical etchability of shear bands in the 2826 alloy was examined by annealing several specimens for 1440 min each at a temperature between 250 and 265° C. The loss of etchability was found to take place at an annealing temperature between 255 and 260° C; a value of 258 ± 2° C being taken as the critical value. An example of shear bands which were no longer chemically attacked is shown in Fig. 4. The annealing temperature was 265° C.

In a second and third sequence of annealing treatments, the respective temperatures were held constant and the time period was altered until the shear bands were no longer etched. The results of these tests indicated that for temperatures of 264 and 272° C, the etchability was lost for annealing periods of 690 ± 30 and 300 ± 30 min, respectively. Based upon the analysis in Section 1 which led to Equation 2, the time–temperature values indicating a loss of chemical etchability were plotted as the natural logarithm of the time against the reciprocal absolute temperature in Fig. 5. A straight line satisfactorily fitted the points, the slope of which gave rise to an apparent activation enthalpy of 250 ± 40 kJ mol^{-1}. A "worst" straight line fit; that is, a line with the largest deviation of slope which still passed through the error bars of the data points, established the absolute error of ±40 kJ mol^{-1}.

Some additional observations are in order. First of all, the etchability of the shear bands found in annealed samples was not as distinct as noted in the as-quenched sample of Fig. 3. Although the chemical etchability of the shear bands in the etchant was verified for annealing periods of 530 and 1060 min at temperatures that went down to 103° C, the shear bands were etched to a gradually decreasing degree as the annealing temperature was increased. Secondly, the temperature interval of 5° C was chosen for those ribbons heat treated for 1440 min between 250 and 265° C because at smaller temperature differences, the point at which etching ceased was more difficult to determine. The cause of the variability was in fact due to differences in the "strengths" of the individual shear bands indicated by differing degrees to which each slip band was chemically attacked. The distribution of the etchability of individual shear bands was less apparent at lower or higher annealing temperatures than at values near the critical point where etchability ceases. This same analysis applied to the absolute error of the time period of annealing (at constant temperature) for the other two points in Fig. 5. Because of the variability of strength of the individual shear bands, the evaluation of the loss of etchability was based upon the response of the majority

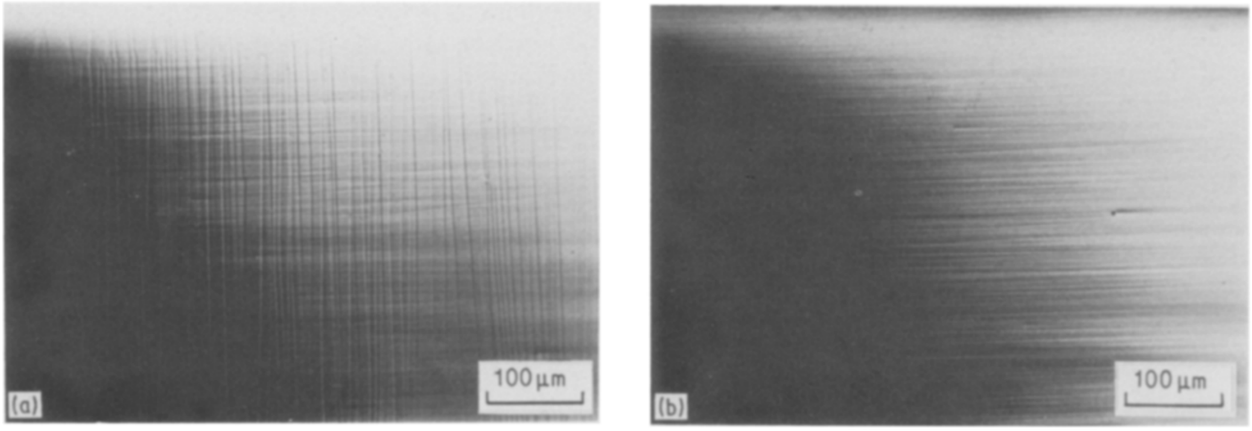

Figure 4 Chemical etchability following annealing at 265° C for 1440 min.

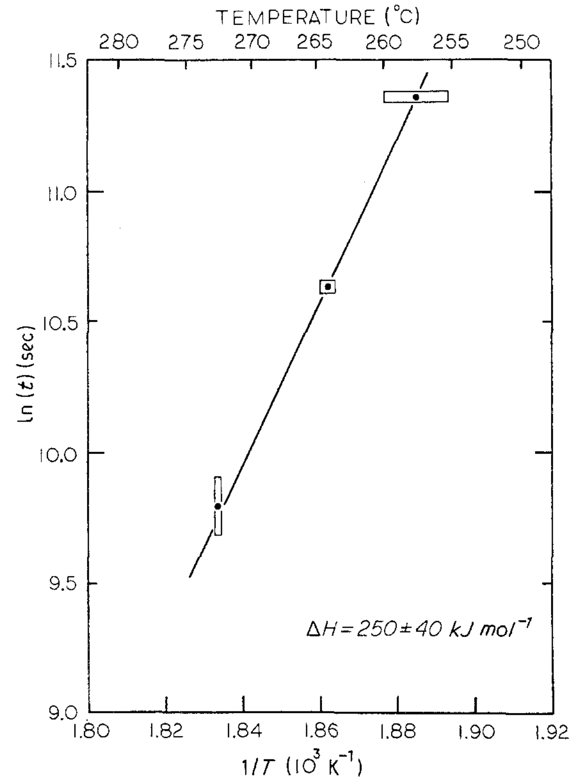

Figure 5 Logarithm of the annealing time plotted against the reciprocal absolute annealing temperature marking the loss of etchability of shear bands in the 2826 alloy immersed in the $CuSO_4$–HCl solution for 5 sec.

of the slip bands in the micrograph. As a final observation it was found to be rather difficult to polish away the etched shear bands. A considerably long period of lapping with a 1.0 μm alumina suspension (more than 10 min) was required to eliminate the evidence of the etched slip bands.

3.2. Electrochemical etching of shear bands

An example of the electrochemical etching of shear bands in a sample of the as-quenched BNi_2 alloy is shown in Fig. 6. Fig. 6a shows the slip steps introduced into the sample which designated the location of the shear bands. The polished and etched sample appears as shown in Fig. 6b. Other than at the shear bands, the etching procedure had no other effect on the material's surface such as pitting, a general tarnish to the surface, nor preferred attack of inclusions present in the matrix. Unlike the case of chemical etching of shear bands discussed in the previous section, the electrolytically etched shear bands were easily polished away with a 0.05 μm alumina suspension (for only 3 min), leaving again a featureless surface. Using sets of photographs similar to Fig. 6, the loss of electrolytic etchability was taken to occur at a temperature of $272 \pm 2°$ C for an annealing time of 500 min. A similar procedure was followed for annealing periods of 1440 and 2880 min. The corresponding temperatures at which etchability was lost were 268 ± 2 and $265 \pm 2°$ C, respectively. Again, the sampling interval of 5° C was based upon the uncertainty in the critical temperature caused by the variable etchability observed for the individual slip bands. The natural logarithm of the annealing time was plotted against the reciprocal absolute annealing temperature; the result is shown in Fig. 7. A straight line that was least-squares fit to the data points resulted in an apparent activation enthalpy of 580 kJ mol^{-1}. A "worst" straight line fit resulted in an absolute error of ± 200 kJ mol^{-1}; the large value being caused by the nominally steep slope to the data.

3.3. Reverse shear of shear bands

The reversibility of shear in shear bands which had been annealed after initial formation in the as-quenched material was evaluated for eleven samples annealed for 500 min at temperature intervals of approximately 16° C in the range of 192 to 375° C. The two sets of photographs for those specimens annealed at 287 and 375° C are shown in Figs. 8 and 9, respectively, and are representative of the overall results. Comparing the slip steps in (a) present after forward bending with those in (b) after the ribbon was straightened out, it was apparent that shear band reversal was not affected by the annealing treatment. Closer examination of the micrographs depicting the reversed deformation revealed that not all of the shear bands had reversed by the same magnitude of forward shear which had originally formed them. As a result, other bands had to take up the additional deformation necessary

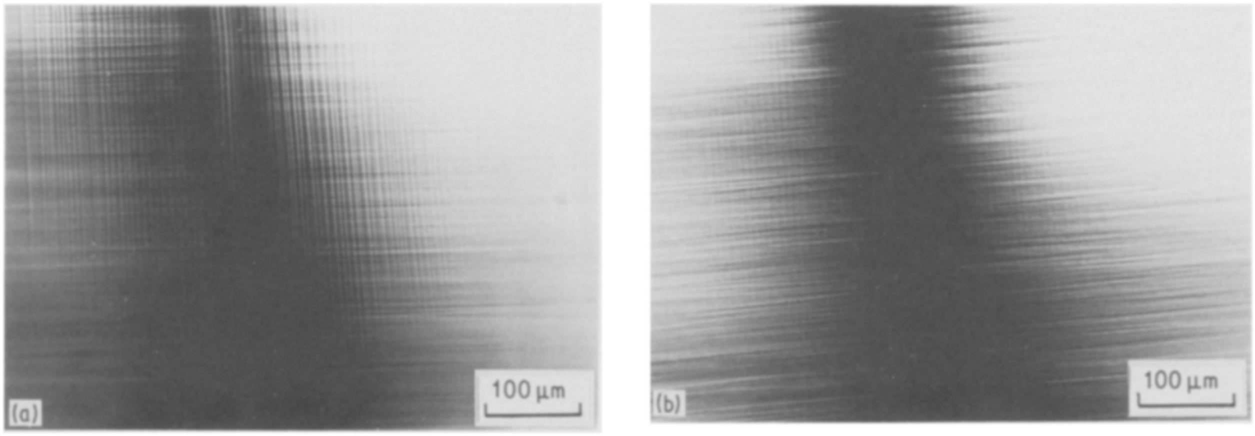

Figure 6 Electrolytic etching of shear bands in the as-quenched BNi_2 alloy using a solution of 21% perchloric acid–acetic acid at a current density of 6.5 mA cm^{-2} and 12° C. (a) Initial slip steps. (b) Etched shear bands on the previously polished surface after 30 min in the electrolyte. (Optical-DIC.)

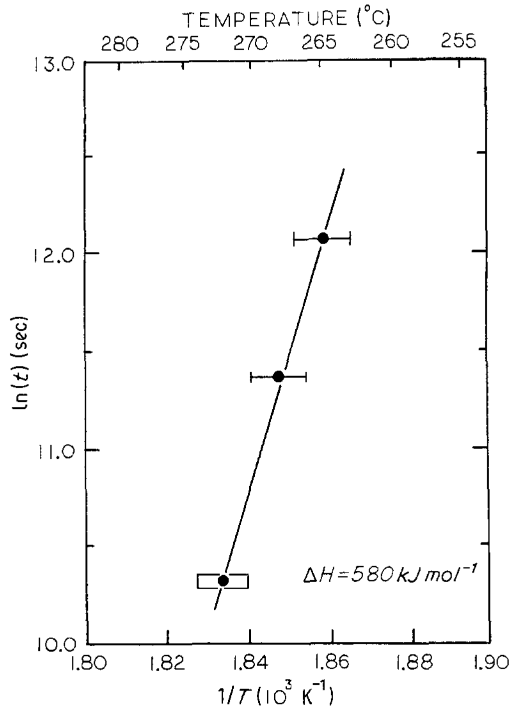

Figure 7 Logarithm of annealing time plotted against the reciprocal absolute annealing temperature marking the loss of electrolytic etchability of shear bands in the BNi_2 alloy.

for the reversed macrostrain of the ribbon, thereby slipping past their initiation points and eliminating the need for the formation of additional shear bands. The size of the slip step did not seem to have an effect on the ability of the accompanying shear band to reverse itself; a point valid in the as-received material as well. Also, the number of shear bands refusing to fully reverse was not a function of the annealing temperature.

Although the vast majority of shear bands slipped backwards to provide the reverse deformation, new slip steps did occur in a few isolated regions. Such cases which appeared in Figs. 8 and 9 were marked by a box. This observation must be qualified in that such new steps were not resolved by the SEM in the pre-annealed photographs. From the micrographs, it was evident that the number of new bands is small and represented isolated incidents rather than a general behaviour. In fact, most samples had no new slip steps created by the reverse deformation.

4. Discussion

4.1. Chemical etchability of shear bands in Metglas 2826

The apparent activation enthalpy describing the loss of chemical etchability of shear bands in the 2826 alloy, 250 ± 40 kJ mol^{-1}, was compared to the activation enthalpies of several thermally activated processes in the 2826 alloy or similar iron–nickel-based metallic glasses: annealing embrittlement, from 88 kJ mol^{-1} for $Fe_{40}Ni_{40}B_{20}$ [10] to 115 kJ mol^{-1} for $Ni_{48}Fe_{29}P_{14}B_2Al_3$ [11]; stress relaxation, 232 kJ mol^{-1} [12]; structural relaxation as indicated by specific heat and X-ray interference function analysis, 155 kJ mol^{-1} [13] and 173 kJ mol^{-1} [14], respectively; and crystallization, from 385 kJ mol^{-1} [15] to 428 kJ mol^{-1} [16]. The activation enthalpy describing the loss of etchability was very close to that of stress relaxation. The immediate conclusion drawn from this similarity was that the chemical etching process was associated with

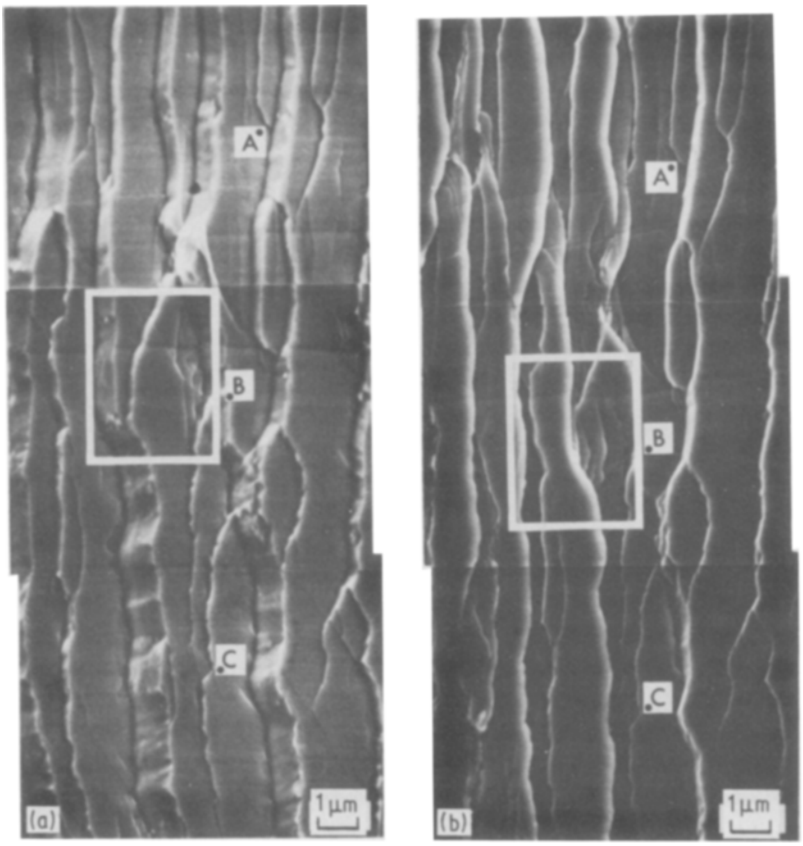

Figure 8 Reversed shear deformation in BNi_2 alloy. (a) Slip steps formed in the as-quenched condition by bending (tensile fibre stresses directed horizontally outwards). (b) The reversed shear of the slip steps following annealing at 287° C for 500 min. (SEM.)

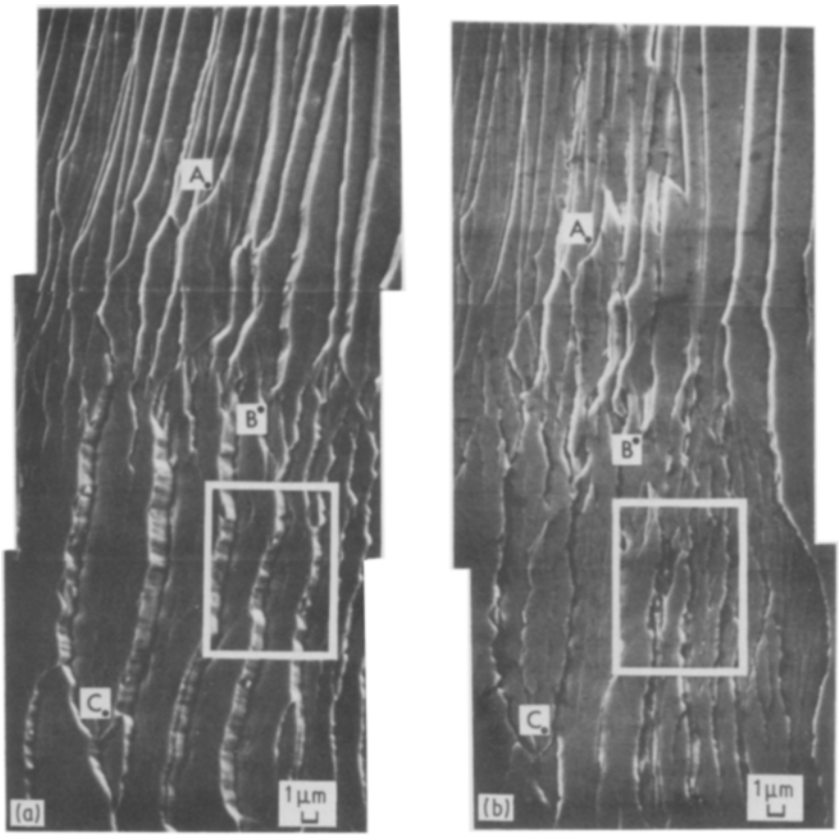

Figure 9 Reversed shear deformation in BNi_2 alloy. (a) Initial slip steps formed in the as-quenched condition. (b) Reversed shear after isothermal annealing at 375° C for 500 min. (SEM.)

a residual stress field accompanying the shear band.

Experimental evidence supporting this possibility will now be presented. First of all, the 2826 alloy has a general susceptibility to cracking in this solution when stressed in tension. A sample of the as-quenched 2826 alloy was bent elastically and immersed in the copper sulphate–hydrochloric acid solution for 30 sec. Fig. 10 shows the surface subjected to the tensile fibre stresses during bending. An extensive formation of cracks (the "dried mud" crack morphology) was observed. When either no stress was present or the stress was compressively elastic, no cracking took place in the material.

Direct observations of the etched shear bands through the use of the scanning electron microscope were made with photographs similar to that shown in Fig. 11. In this case, the sample was deformed, annealed at 103° C for 1060 min, the shear steps were polished away, and the ribbon then etched in the copper sulphate–hydrochloric acid solution. Severe gaps have been formed at the location of the shear bands. Reviewing the entire region of deformation via photographs similar to that of Fig. 11 determined that the various strengths or degrees of etching of the shear bands actually reflected the different extents of the widths of the fissures observed at the respective shear bands. In nearly all cases, the left- and right-hand sides of the fissures could be matched exactly. Therefore, these fissures were not caused by the gross dissolution of material but rather were likely the result

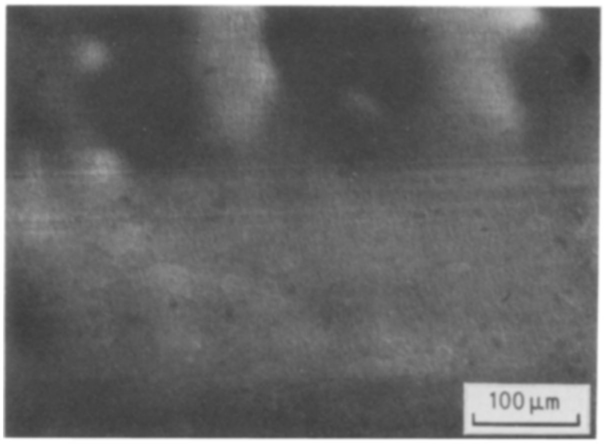

Figure 10 Cracking on the tensile side of an elastically bent ribbon of 2826 simultaneously immersed in the $CuSO_4$–HCl solution for 30 sec. (Optical-DIC.)

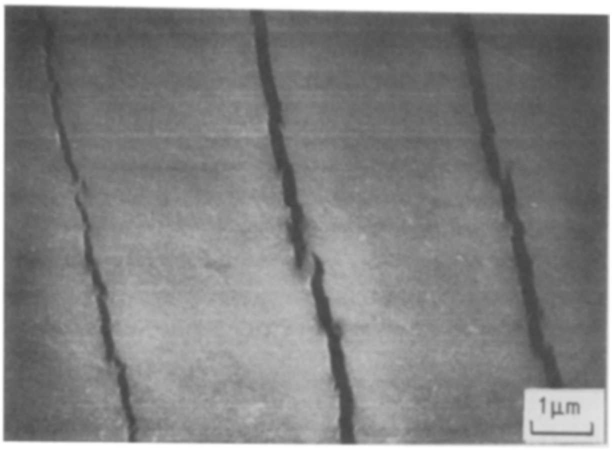

Figure 11 Chemical attack of shear bands, the steps of which were polished away, of a 2826 sample annealed at 103° C and 1060 min by the $CuSO_4$–HCl solution. (SEM.)

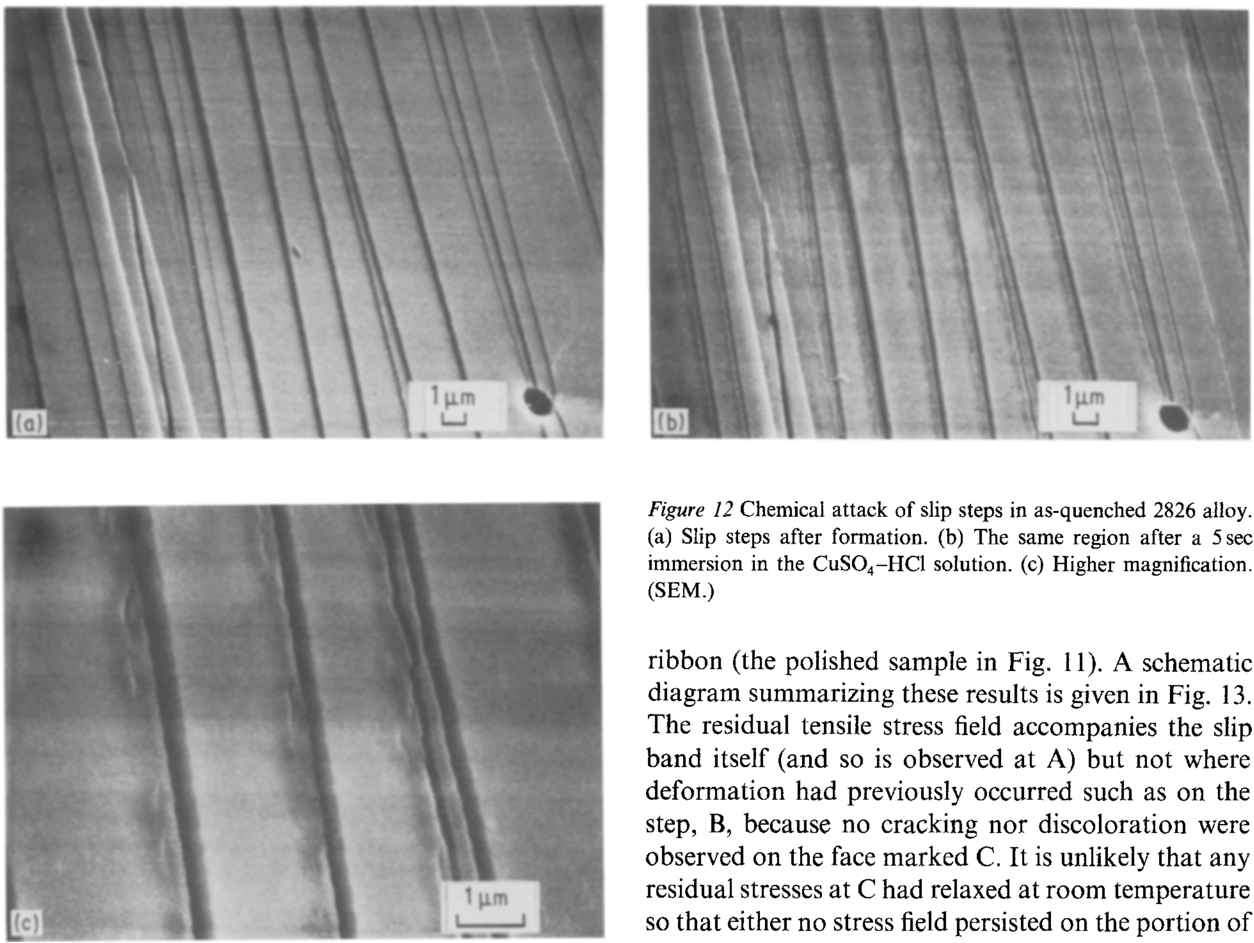

Figure 12 Chemical attack of slip steps in as-quenched 2826 alloy. (a) Slip steps after formation. (b) The same region after a 5 sec immersion in the $CuSO_4$–HCl solution. (c) Higher magnification. (SEM.)

of the opening up of the cracks formed at the bands. This observation would lead to the conclusion that the etching process was a form of stress corrosion cracking.

Additional evidence to this effect appears in Fig. 12. Fig. 12a shows the slip steps introduced into a ribbon of as-quenched 2826 alloy. Then, without polishing the surface, the specimen was immersed in the copper sulphate–hydrochloric acid solution. The etched slip steps appear in Fig. 12b and at a higher magnification in Fig. 12c. A discoloration, together with small cracks, was found on that side of the slip step which was displaced towards the neutral axis of bending. The size of the discoloration zone (which was caused by a heavier than normal oxidation of the metal surface) scaled roughly with the size of the slip step. Similar areas of heavy oxidation had been noted in the crown of deformed material surrounding a microhardness indentation in the same alloy following immersion in the above etchant. Therefore, the discoloration of the slip steps represented residual stresses of the material next to the step although other investigators [17] may take that as evidence of homogeneous deformation accompanying inhomogeneous flow in metallic glasses. The presence of the small cracks running parallel to the slip step provided a direct indication of a tensile stress component perpendicular to the shear band in that region. Comparing Figs 11 and 12, it was concluded that the extent of deformation and the residual stress field accompanying the slip band was much greater near to the surface of the ribbon (Fig. 12) than further towards the inside of the ribbon (the polished sample in Fig. 11). A schematic diagram summarizing these results is given in Fig. 13. The residual tensile stress field accompanies the slip band itself (and so is observed at A) but not where deformation had previously occurred such as on the step, B, because no cracking nor discoloration were observed on the face marked C. It is unlikely that any residual stresses at C had relaxed at room temperature so that either no stress field persisted on the portion of the step noted by B, or that the residual stress components located there were compressive in nature.

Interestingly enough, in the transmission electron micrographs of shear bands by other authors (e.g. Fig. 3 of [18]), the brighter contrast of the slipped material extended into the same region of the shear step as where the residual stress field was located through the etching experiments. It did not exist symmetrically at the other side of the slip band.

In conclusion, the presence of a residual stress field accompanying shear bands in metallic glasses seems to be a likely cause for the chemical etching effect.

4.2. Electrochemical etching of shear bands

The apparent activation enthalpy for the loss of electrochemical etchability of shear bands in the BNi_2 alloy was $580\,\mathrm{kJ\,mol^{-1}}$. This value is very high compared to those describing structural relaxation, annealing embrittlement, creep deformation and stress relaxation. The preferred electrochemical attack of the slip bands was not a form of stress corrosion cracking. Aside from the dissimilar activation enthalpies, the

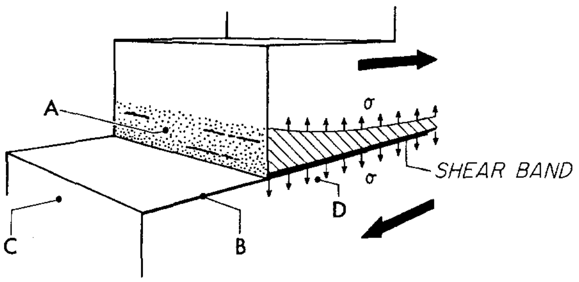

Figure 13 Schematic representation of the extent of a residual tensile stress component about a shear band.

electrolytically etched shear bands were easily polished away. This fact was confirmed in the 2826 alloy by electroetching slip bands in that material (same electrolyte; 6.0 mA cm^2; 15 min) as well. Without the applied voltage, the electrolyte did not attack the deformed areas. Therefore, the electrochemical etching process is apparently a property of the deformed material constituting the band. Similar high-nickel amorphous alloys have demonstrated apparent activation enthalpies for crystallization in close proximity to the 580 kJ mol^{-1} number (e.g. $\Delta E = 627$ kJ mol^{-1} for $Ni_{75}P_{16}B_6Al_3$ [19]). This comparison does not suggest that the loss of etchability was necessarily described by exactly those mechanisms responsible for crystallization. However, it does indicate that more complex atomic rearrangements took place during thermal annealing to reduce the etching strength of the shear bands.

The fact that the shear band was more anodic than the bulk material may have resulted from a greater degree of disorder (either chemical, topological, or both) theorized to exist in the deformed regions. Indirect evidence that inhomogeneous deformation creates regions of increased topological disorder stems from the X-ray structure factor analysis of cold-rolled metallic glass ribbons [20] in which the decrease in height and broadening of the peaks indicate a lower degree of order in the material. As a result, the effect of the heat treatment would have been to reduce the amount of disorder in the deformed region and thereby decrease the electrical potential difference between the band and the bulk of the specimen resulting in a decrease of etchability.

An important point which must be recalled is that the loss of etchability did not provide an absolute scale of the presence of the shear bands. For example, the sample annealed at 287° C for 500 min did not reveal any shear bands when etched with a current density of 6.5 mA cm^{-2}. However, increasing the etching current density to 10 mA cm^{-2} (the upper limit current density above which the polishing mechanism took over) did electrolytically etch the slip bands. Therefore, at a set of given cell parameters (current density, time, electrolyte temperature, etc.), only relative changes in the etchability of the slip bands could be determined which are all that is necessary to calculate the apparent activation enthalpy.

4.3. Reverse shear behaviour of shear bands

The shear bands formed prior to thermal annealing were able to support the reverse deformation after heat treatment without the need of additional shear bands. Therefore, the specified heat treatments did not fully recover the properties of the deformed material to those before the deformation. The number of shear bands reluctant to completely reverse was found not to be correlated to the heat-treatment parameters nor to the size of the accompanying surface step. Therefore, this behaviour was not the result of structural changes to the shear band arising from the annealing treatment but was probably caused by simply a statistical chance where some bands reversed first and to a larger extent than when initially formed, thereby reducing the necessary reverse shear exhibited by other bands. The same random reversal of the shear bands may have caused local stress concentrations which gave rise to new shear bands in some isolated regions, assuming that they were not present prior to heat treatment.

The heat treatment did not remove the identity of the shear bands which distinguished them from the undeformed material. A similar situation was examined by Swann [21] with regard to the transgranular stress corrosion cracking of deformed single-phase binary crystalline alloys. A decrease in the susceptibility of cracking after heat treatment was believed to have been caused by a return of the order which was destroyed by the passage of dislocations along slip planes and which gave rise to the chemical attack. However, the dislocation structures which identified the slip band were still present after heat treatment. The same circumstances may apply as well to the effect of heat treatment on shear bands in metallic glasses. The disorder created in the zones of intense deformation was partially eliminated by the annealing procedure so as to reduce the electrochemical attack of the bands. However, the plastically deformed region was not entirely returned to the likeness of the bulk material so that further deformation continued to take place there.

5. Conclusions

1. Shear bands in Metglas 2826 were susceptible to chemical etching by immersion of the ribbon in a 50 ml HCl–5 ml H_2O–10 g $CuSO_4$ solution at room temperature.

2. The chemical etchability property could be eliminated by the thermal annealing of the sample for specific time and temperature parameters. An Arrhenius dependence between those two variables gave an apparent activation enthalpy of 250 kJ mol^{-1}. This value was very close to that describing stress relaxation in this alloy.

3. The apparent activation enthalpy together with direct visual evidence suggests that the chemical etching of the slip bands was actually stress corrosion cracking due to a residual stress field of the shear bands.

4. The electrolytic etching of shear bands in the deformed BNi_2 alloy using a 21% perchloric acid–79% acetic acid electrolyte at 12° C could be eliminated by thermal annealing of the specimen. The apparent activation enthalpy was 580 kJ mol^{-1}; a value comparable to that describing a more complex atomic rearrangement such as found in crystallization.

5. Similar to other metallic glass alloys, the slip along shear bands formed on the tension side of a bent BNi_2 alloy ribbon (as-quenched) could be reversed by bending the ribbon backwards. As a result, no additional shear bands formed during the reverse bending.

6. Thermal annealing of specimens with shear bands introduced in the as-quenched condition for 500 min at temperatures in the range of 192 to 375° C had no effect on the reversibility of slip in the deformation bands.

Acknowledgements

We wish to thank Dr Lance Davis of Allied Signal, Incorporated, for providing the material and a fellowship to one of the authors (PTV). Additional funding by the Department of Energy under contract DE-FG02-85ER45201 is gratefully acknowledged. This paper is based on part of the PhD thesis completed by Paul Vianco at the University of Rochester (1986).

References

1. P. DONOVAN and W. STOBBS, *Acta Metall.* **29** (1981) 1419.
2. C. PAMPILLO, *Scripta Metall.* **6** (1972) 915.
3. H. CHEN, H. LEAMY and M. O'BRIEN, *ibid.* **7** (1973) 415.
4. W. PARKINS, G. DENIS and F. BROWN, *J. Appl. Phys.* **22** (1951) 1012.
5. C. PAMPILLO, *J. Mater. Sci.* **10** (1975) 1194.
6. C. PAMPILLO and H. CHEN, *Mater. Sci. Eng.* **13** (1974) 181.
7. X. CAO and J. C. M. LI, *Acta Metall.* **33** (1985) 499.
8. "Metals Handbook", 8th Edn, Vol. 8 (ASM Metals Park, Ohio, 1973) p. 101.
9. *Ibid.*, p. 26.
10. R. CHI, H. CHEN and C. MILLER, *J. Appl. Phys.* **49** (1978) 1715.
11. C. PAMPILLO and D. POLK, *Mater. Sci. Eng.* **33** (1978) 275.
12. D. AST and D. KRENITSKY, *J. Mater. Sci.* **14** (1979) 287.
13. H. CHEN, *J. Appl. Phys.* **52** (1981) 1868.
14. T. EGAMI, *J. Mater. Sci.* **13** (1978) 2587.
15. M. SCOTT, *ibid.* **13** (1978) 291.
16. T. WATANABE and M. SCOTT, *ibid.* **15** (1980) 1131.
17. P. ZIELINSKI and D. AST, *Philos. Mag. A* **48** (1983) 811.
18. P. DONOVAN and W. STOBBS, *Acta Metall.* **31** (1983) 1.
19. E. COLEMAN, *Mater. Sci. Eng.* **23** (1976) 161.
20. W. GUON, N. COWLAM and M. GIBBS, *J. Mater. Sci.* **19** (1984) 1374.
21. P. SWANN, *Corrosion* **19** (1963) 1026.

Received 29 July 1986
and accepted 15 January 1987