

## STORED ENERGY OF THE DEFORMED METALLIC GLASS $\text{Ni}_{78}\text{Si}_8\text{B}_{14}$

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### SUMMARY

The stored energies and the crystallization behaviour of the metallic glass  $\text{Ni}_{78}\text{Si}_8\text{B}_{14}$  are compared by Differential Scanning Calorimetry (DSC) for as-received and deformed samples. The deformation of the latter is achieved by multiple passes through a miniature rolling mill. Two measuring procedures for the DSC-runs are presented and compared with respect to the results for the stored energy.

### INTRODUCTION

During deformation of crystalline, pure metals about 5-10% of the deformation work will be stored in the material while the rest is dissipated as heat. The stored work is contained in a large number of lattice defects which are produced during deformation in the initially nearly defect free structure. The most important defects are vacancies and dislocations. Both locally distort the crystal lattice and store energy analogous to an elastically strained spring. Increasing the temperature this stored energy is released when the distorted structure recrystallizes and a new, nearly defect free lattice is formed (ref.1). The energy balance of this process can be followed by calorimetry.

Amorphous metals however do not show a regular, periodic arrangement of the atoms. They are in a glasslike state, where the sites of the atoms are only correlated over a short distance. The concept of a dislocation as in crystalline material cannot be applied and defects of the vacancy type are probably not stable in an amorphous structure but dissolve in a diffuse way as computer simulations (ref.2) imply.

Nevertheless some measurements (ref.3,4,5) suggest that deformed metallic glasses do contain stored energy due to the deformation process. Using the amorphous alloy VITROVAC 0080 ( $\text{Ni}_{78}\text{Si}_8\text{B}_{14}$ ), supplied by Vakuumschmelze, Hanau, FRG, an attempt is made to quantify calorimetrically changes in the crystallization behaviour as well as the stored energy in this material after cold rolling. Since specimens of the material show a rather wide variation in their thermal behaviour (probably due to variations in the thermal history of

different specimens) compared with the small additional heat flow when the stored energy is released, the results of two measuring procedures will be described.

#### EXPERIMENTAL DETAILS

Ribbons of the metallic glass  $\text{Ni}_{78}\text{Si}_8\text{B}_{14}$  (width 5.8mm, thickness  $63\mu\text{m}$ ) have been deformed in a miniature rolling mill (ref.6) by multiple passes by about 52% (final thickness  $31\mu\text{m}$ ). After cutting the deformed ribbons up and cleaning in ethanol the pieces were stored in a fridge until being measured with a Perkin-Elmer DSC 7. Also undeformed specimens otherwise treated the same way were investigated. Each DSC-run used about 40mg of material and was carried out under flowing nitrogen gas.

Two measuring procedures were tried: using method 1, where the reference state was the crystalline state of the same sample, the specimens started at 303K and went up to 803K with a heating rate of either 40, 20, 10 or 1 K/min. During this ramp the samples crystallized. This was followed by a fast cooling back to 303K and a repetition of the first part. The difference of the two heating ramps was then taken as the result. Fig. 1 shows the result of one experiment with an undeformed sample starting in an as-received state.

During method 2 the specimens started at 303K and went up to  $T_1$ , which was either 523K, 598K, 673K or 723K, all runs with a heating rate of 10K/min. This was followed by a fast cooling back to 303K and a subsequent heating run with 10K/min to 803K. The difference of the two heating runs in the range 303K to  $T_1$  was then taken as the result.

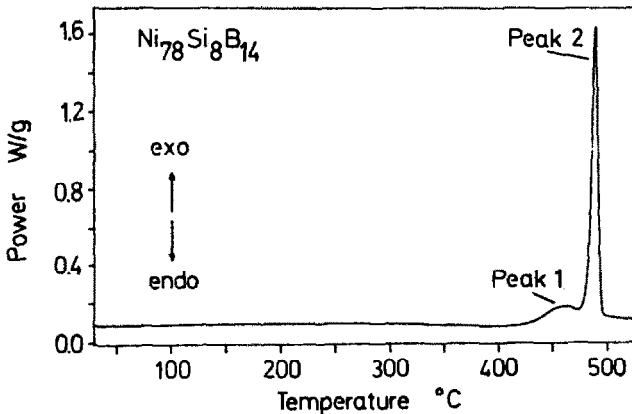


Fig.1: The result of a DSC-run with an undeformed specimen following method 1 ( $\dot{T}=10\text{K/min}$ ).

## RESULTS

The two exothermic peaks in Fig.1 suggest that crystallization in this metallic glass takes place in two stages. Defining the crystallization temperature as temperature at the maximum of each peak, Fig.2 plots the crystallization temperature of both peaks for a number of deformed and undeformed specimens. A considerable spread, in particular for the crystallization temperature of peak 1, can be noticed. However the mean value of either peak does not show a clear change with deformation. A similar result follows for the

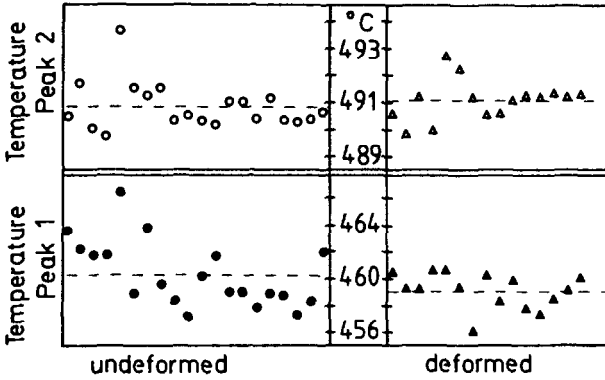


Fig.2: The temperature of the maximum of both crystallization peaks for a number of undeformed and deformed specimens ( $\dot{T}=10\text{K/min}$ ). The mean is indicated by the dashed line.

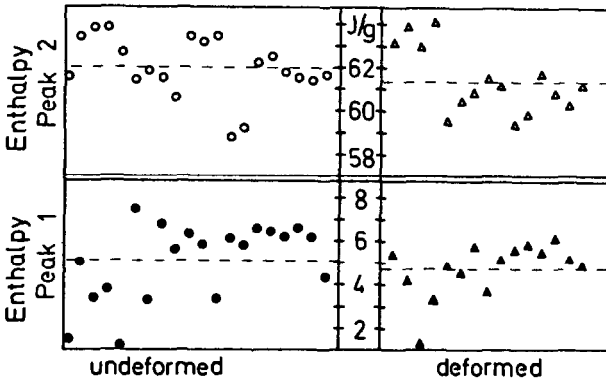


Fig.3: The crystallization enthalpy of both crystallization stages for a number of undeformed and deformed specimens ( $\dot{T}=10\text{K/min}$ ). The mean is indicated by the dashed line.

crystallization enthalpy of both peaks as shown in Fig.3. Again the mean value does not indicate any change with deformation.

Analysing the crystallization temperatures for different heating rates the Kissinger method will give the activation energy of both crystallization stages. With the present data this is indeed the case for the second crystallization stage. Both the deformed and undeformed specimens lead to an activation energy of 3.7 eV/atom. However for the first peak the experimental points do not fall onto a straight but curved line in the Kissinger plot. Hence no activation energy independent of heating rate can be given for that peak.

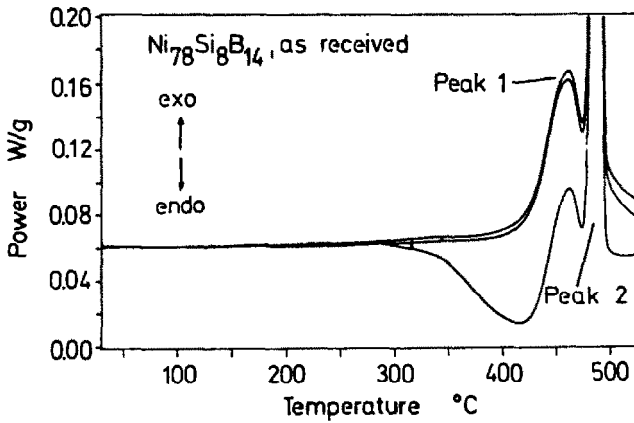


Fig.4: The results of three representative DSC-runs following method 1 for undeformed specimens ( $\dot{T}=10\text{K/min}$ ).

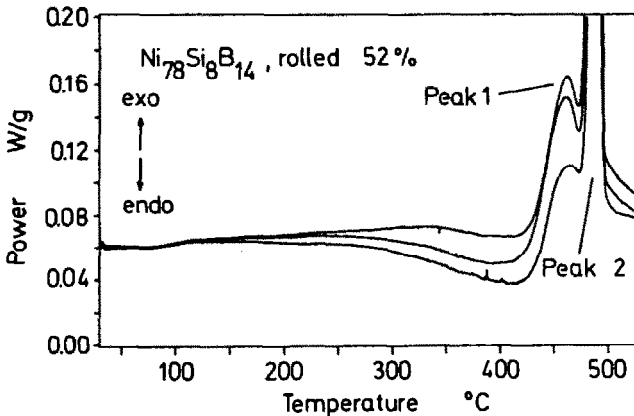


Fig.5: The results of three representative DSC-runs following method 1 for deformed specimens ( $\dot{T}=10\text{K/min}$ ).

Fig.4 and Fig.5 compare the heat flow balance of three traces of undeformed and deformed specimens following method 1. There is considerable scatter with respect to reproducibility within each group. This is not due to the calorimeter but to the chosen method and variations within the specimens, maybe caused by compositional variations or differing quenching conditions/thermal histories. Nevertheless a difference of the heat flow between undeformed and deformed specimens is noticeable starting at about 80°C with a distinct increase of the heat released by the deformed specimens. How far this additional heat release extends in temperature can not be determined due to the considerable scatter.

Fig.6 shows the equivalent experimental results for specimens measured following method 2. Considering the much more sensitive scale the scatter within each group appears much smaller. While for the undeformed samples the heat flow remains constant up to about 200°C, for the deformed samples from about 80°C a distinct increase of the heat flow starts to develop. Taking an average for each group, the two curves can be shifted vertically so that the low temperature parts, where no reaction is expected, coincide. Now it can be seen (Fig.7) that the deformed specimens release stored energy in the temperature range from 80°C to 380°C. The area marked corresponds to an energy of 445 J/mol.

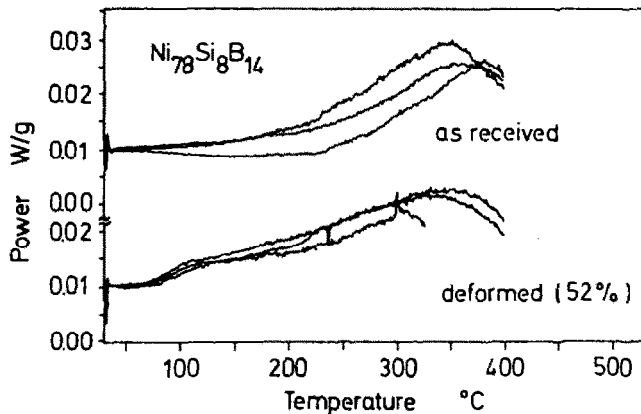


Fig.6: The results of DSC-runs following method 2 for three representative undeformed und deformed specimens ( $\dot{T}=10\text{K/min}$ ).

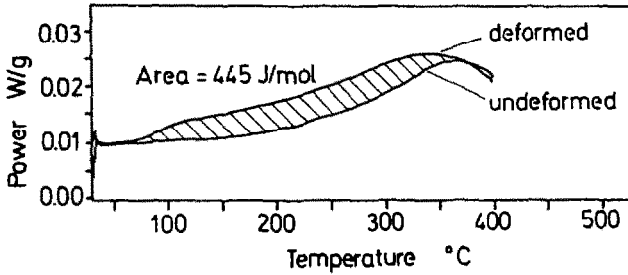


Fig.7: Averaged DSC-curves from Fig.6 shifted to coincide in the low temperature range. The shaded area represents the average stored energy due to the rolling deformation.

## DISCUSSION

The specimens investigated show a considerable variation of behaviour so only trends based on averages can be given. Deformation does not seem to influence the crystallization. The position of the crystallization peak as well as its enthalpy remain unaffected. A similar result for the peak position comes from measurements of the internal friction in the same material (ref.7). Other metallic glasses (ref.4) show this behaviour as well. The insensitivity of crystallization towards a preceding deformation is also reflected in the unchanged activation energy of peak 2 after deformation.

To peak 1, which is more likely to be affected by deformation since it represents the initial crystallization stage, however a defined activation energy cannot be assigned. This though is not due to a difference between deformed and undeformed specimens, in fact the corresponding Kissinger plots are nearly identical, but is probably caused by a third reaction stage which is also hidden in peak 1. This will have to be investigated further.

The stored energy due to deformation shows up more clearly using method 2 which compares two amorphous states. Method 1 with the inclusion of the strongly exothermic crystallization reaction seems to lead to changes in the thermal behaviour of the samples which partly cover up the results for the stored energy. The total stored energy of 445J/mol at a rolling deformation of about 52% is large compared with e.g. about 57J/mol for crystalline copper rolled 92%. However in the latter case all energy is released over an interval of about 30K while with the metallic glass  $\text{Ni}_{78}\text{Si}_8\text{B}_{14}$  the energy release extends over at least 300K. This suggests that unlike in the crystalline material where mainly one single type of defect is responsible for the storage of energy, namely dislocations, in metallic glasses either a large number of defect types or one type in a continuously varying form is involved.

As Fig.8 demonstrates  $\text{Ni}_{78}\text{Si}_8\text{B}_{14}$  deforms inhomogeneously during rolling by

shear in irregular bands about 0,5-1 $\mu$ m apart. These shear bands represent highly ductile zones (which can be seen in particular on fracture surfaces) with a width of about 10-20nm according to ref.8. Electronmicroscopical investigations of the shear band structure (ref.8) suggest that during deformation not so much a change in structure but the creation of elastic strain fields takes place. Those elastic strain fields, the structure of which is still uncertain, seem to be responsible for most of the property changes observed in deformed metallic glasses e.g. the magnetic pin effect. Presumably the energy released during calorimetric measurements also originates from these elastic strain fields.

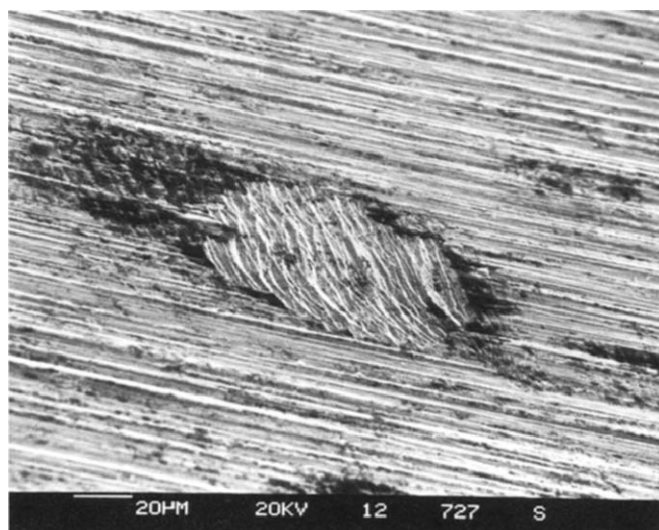


Fig.8: Shear bands at the bottom of a depression on the surface of a rolled metallic glass ribbon. Higher magnification shows that the shear bands are 0,5-1  $\mu$ m apart.

However, as can be seen from the traces of the undeformed material, there is already an energy release in the as-received state starting at about 200°C. This is due to the so called structural relaxation, where thermally activated atomic rearrangements presumably reduce the elastic strains quenched in during the production process. Whether there is a principal difference between those strain fields introduced during deformation and those already contained in the as-quenched material is not clear at this stage and requires further investigations.

## ACKNOWLEDGEMENTS

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## REFERENCES

- 1 F.Haeßner, Recrystallization of Metallic Materials, 2nd edn., Dr.Riederer-Verlag, Stuttgart, FRG, 1978.
- 2 P.Chandhari et al., Computer simulation studies of defects and atomic transport, in: H.Beck, H.-J.Güntherodt (Eds.), Glassy Metals II, Springer Verlag, Berlin, 1983.
- 3 H.S.Chen, Stored energy in a cold-rolled metallic glass, *Appl.Phys.Lett.* 29 (1976) 328.
- 4 D.Akhtar, R.P.Mathur, Energy release on heating of a deformed amorphous alloy, *Z.Metallkde* 78 (1987) 738.
- 5 G.Stergioudis, P.Rentzeperis, Released energy during heating of two deformed amorphous alloys of the Cu-Zr system, *Z.Metallkde* 77 (1986) 54.
- 6 F.Haeßner, A.Speitling, Kaltwalzen von Bändern aus amorphen Metallen, *Z.Metallkde* 74 (1983) 763.
- 7 H.-R.Sinning, F.Haeßner, Influence of cold rolling on the internal friction during crystallization of some metal-metalloid glasses, in *Proc. of the 5th Int.Conf. on Rapidly Quenched Metals*, Würzburg, FRG, September 1984, North Holland Physics Publishing, Amsterdam, 1985, p.243.
- 8 P.E.Donovan, W.M.Stobbs, The structure of shear bands in metallic glasses, *Acta Met.* 29 (1981) 1419.