

**MECHANICALLY ALLOYED ODS STEEL & Ni-BASE SUPERALLOY
- A STUDY OF DIRECTIONAL RECRYSTALLISATION USING DSC**

K. Mino, H. Harada, H.K.D.H. Bhadeshia (a) and M. Yamazaki (b)

(a) University of Cambridge/JRDC, Dept. of Materials Science and
Metallurgy, Pembroke Street, Cambridge CB2 3QZ UK

(b) National Research Institute for Metals/JRDC
2-3-12 Nakameguro, Meguro-ku, Tokyo 153, Japan

ABSTRACT

A precision differential scanning calorimeter (DSC) has been used to characterise the directional recrystallisation behaviour of mechanically alloyed, oxide dispersion strengthened steel (*MA956*) and nickel-base superalloy (*TMO-2*) with the aim of revealing details about the mechanism of recrystallisation.

It is common practice to associate the onset of recrystallisation in ODS alloys during continuous heating with a well defined "recrystallisation temperature", a parameter implied to be a characteristic of the as-received material. Our experiments on MA956 (a mechanically alloyed and yttrium oxide dispersion strengthened steel) show that during continuous heating ($5\text{-}40^\circ\text{C min}^{-1}$), the recrystallisation process occurs over a temperature interval as large as 100°C . Furthermore, the temperature at which crystallisation begins appears to be sensitive to the heating rate. The results are not surprising when interpreted in terms of reaction rate theory, if it is assumed that very little recovery occurs during heating elevated temperatures. Evidence is presented to demonstrate that this is the case, and the results are interpreted using kinetic theory whose form predicts that recrystallisation should be retarded as the heating rate is increased.

TMO-2 is a mechanically alloyed, yttrium oxide dispersion strengthened nickel-base superalloy with the important characteristic that there is a significant temperature interval between γ' solution and the onset of directional recrystallisation. This facilitates the easier interpretation of DSC data with little interference between the endothermic γ' solution and exothermic stored energy release processes.

INTRODUCTION

Two of the most important alloy systems to emerge from the mechanical alloying process [1] are based on iron and nickel [see for example 2-8]. The solid-state alloying process for these materials is designed to introduce fine dispersions of yttrium oxide particles. A variety of alloying elements are also introduced, which further improve the elevated temperature properties such as strength, oxidation and hot-corrosion resistance. The mixtures of metal powders and fine refractory oxide powders are milled together, extruded, and further deformed to achieve the required shape. At this stage of the process the alloys are found to be very hard, even though the extrusion of other deformation processes essential for consolidation are generally carried out at temperatures in excess of 1000°C .

The purpose of the present work was to investigate, using calorimetry, the changes that take place when the deformed alloys are heat-treated in order to produce softening and

recrystallised microstructures. Two particular alloy systems are examined, *MA956* which is a mechanically alloyed yttrium oxide dispersion strengthened steel, and *TMO-2* which is a mechanically alloyed nickel-base superalloy also containing yttrium oxide. Both of these alloys, during heat-treatment following the deformation processing, end up with an extremely anisotropic microstructure consisting of highly elongated coarse grains pointing along the original extrusion direction. It is important to understand the factors controlling such behaviour, and the work presented here is a part of a larger programme leading to the modelling of microstructural development during directional recrystallisation.

EXPERIMENTAL TECHNIQUES

Incoalloy *MA956* is a ferritic stainless steel fabricated by charging three primary powders, elemental iron, a pre-alloyed chromium rich master alloy, and yttria into a water-cooled vertical attritor. The consolidation of the resultant mechanically alloyed powder is achieved by extrusion in a mild steel can to a bar of 65 mm diameter. The canning material is removed by machining prior to rolling. The bar is then hot-rolled at 1000°C to reduce the diameter to 25 mm. Alloy *TMO-2* is produced similarly but was extruded at 1050°C (extrusion ratio 15:1) and at a speed of 400 mm s⁻¹.

Table 1: Chemical composition (wt%) of the alloys used in this investigation.

	C	Al	Ti	Cr	Mo	Co	W	Ta	B	Zr	Y ₂ O ₃	Balance
<i>MA956</i>	0.01	4.5	0.5	20.0	0.5	-	-	-	-	-	0.5	Fe
<i>TMO-2</i>	0.05	4.2	0.8	5.9	2.0	9.7	12.4	4.7	0.01	0.05	1.1	Ni

Differential scanning calorimetry was carried out using a *Netzsch DSC 404/3/413/D* machine which is a specially designed high-temperature, heat flux DSC with computer control and data acquisition. It uses a Pt/Rh furnace which has very low temperature gradient characteristics. The sample and reference are placed in thermally balanced Pt crucibles. Any event leading to differences in heat evolution or heat capacity between the sample and the reference cause a signal, which can be interpreted to reveal thermodynamic data associated with the event.

Calorimetric measurements were carried out during continuous heating (5-40 K min⁻¹), the sample mass typically at about 200 mg. A reference of comparable mass was used, made of the same alloy as the sample, but in an already recrystallised condition. This led to a very significant improvement in accuracy, as illustrated in Figure 1, where a comparison is made between DSC runs in which the reference container was either empty or contained the recrystallised sample. In all cases, the samples were examined using light microscopy, to confirm recrystallisation. All the experiments were carried out using an argon atmosphere in the DSC chamber.

RESULTS AND DISCUSSION

MA956

The results of differential scanning calorimetric experiments conducted at a variety of heating rates are presented in Figure 2. It is evident (Figure 2a) that recrystallisation occurs over a range of temperatures and that the recrystallisation rate varies with the rate of heating. Indeed, the process is clearly retarded to higher temperatures as the heating rate is increased. Because of the high temperatures involved, and since the recrystallisation is spread over a range of temperatures, the signal to noise ratio for the exothermic peaks is on average about five, so that the error in peak area measurements is expected to be rather large, estimated at

5 K min⁻¹ to be $\pm 20\%$. For the same reasons, errors are expected in the measurement of the temperatures where recrystallisation is initiated (T_I) and where it is completed

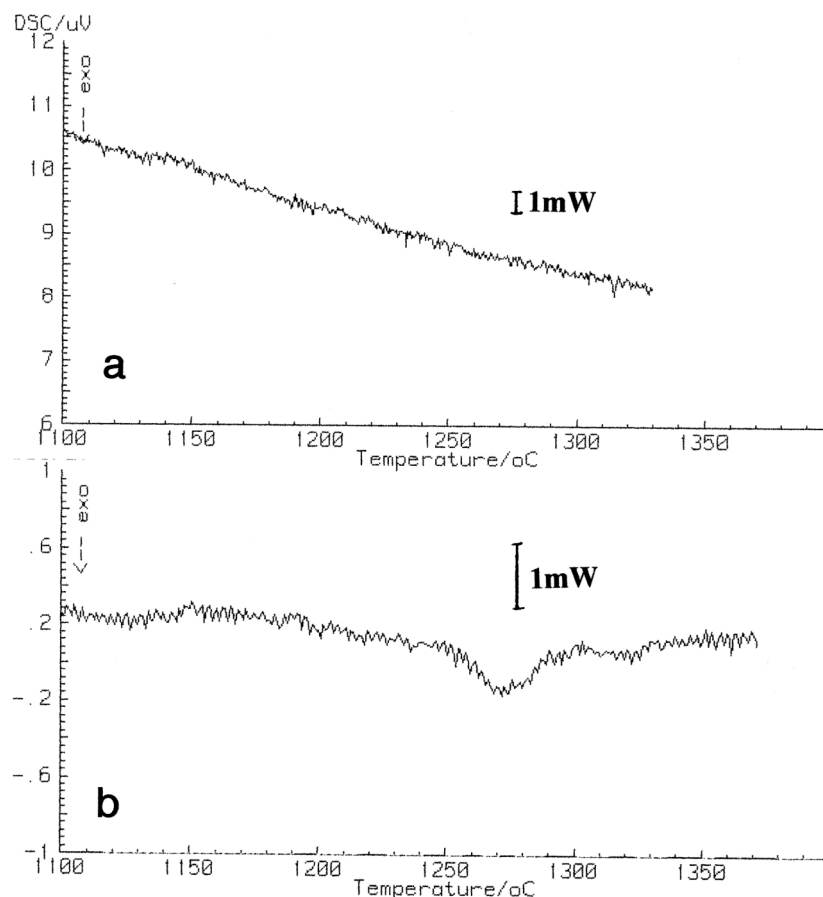


Fig. 1: DSC curves of *MA956* heated at 10 K min⁻¹. (a) Empty reference crucible, (b) Reference consisting of a recrystallised specimen of *MA956*; the curve illustrates the evolution of heat as the test sample in the sample pan undergoes recrystallisation.

(T_C). To check the magnitudes of the latter errors, the DSC data were compared with the hardness changes during recrystallisation (Fig. 2b). To measure the hardness at any stage of recrystallisation samples were cooled (by switching off the radiant furnace) from a variety of temperatures, many of them being in a partially recrystallised state. For a heating rate of 20 K min⁻¹, these data indicate that DSC measured T_I is an overestimate by about 15°C, whereas T_C is similarly underestimated by about 20°C.

These difficulties are expected to become more pronounced as the heating rate is increased. The temperature range over which recrystallisation occurs ($T_C - T_I$) is found to increase as a function of the heating rate (Figure 3). This in turn means that the exothermic peak due to the release of stored energy during recrystallisation becomes more diffuse. Consequently, the measured enthalpy change *appears* to decrease with the heating rate, because the background noise then becomes increasingly significant (Fig. 3b). It is also possible that recrystallisation remains incomplete at large heating rates, but for the range of rates utilised here (5-40 K min⁻¹), recrystallisation was always found to be complete when the samples were examined using light microscopy. Thus, the apparent decrease in the recrystallisation

enthalpy is believed to be an artefact of the decrease in the signal to noise ratio. It is also possible that small regions of the sample remain unrecrystallised at the larger heating rates, although hardness and light microscopy revealed that this must be a rather small effect.

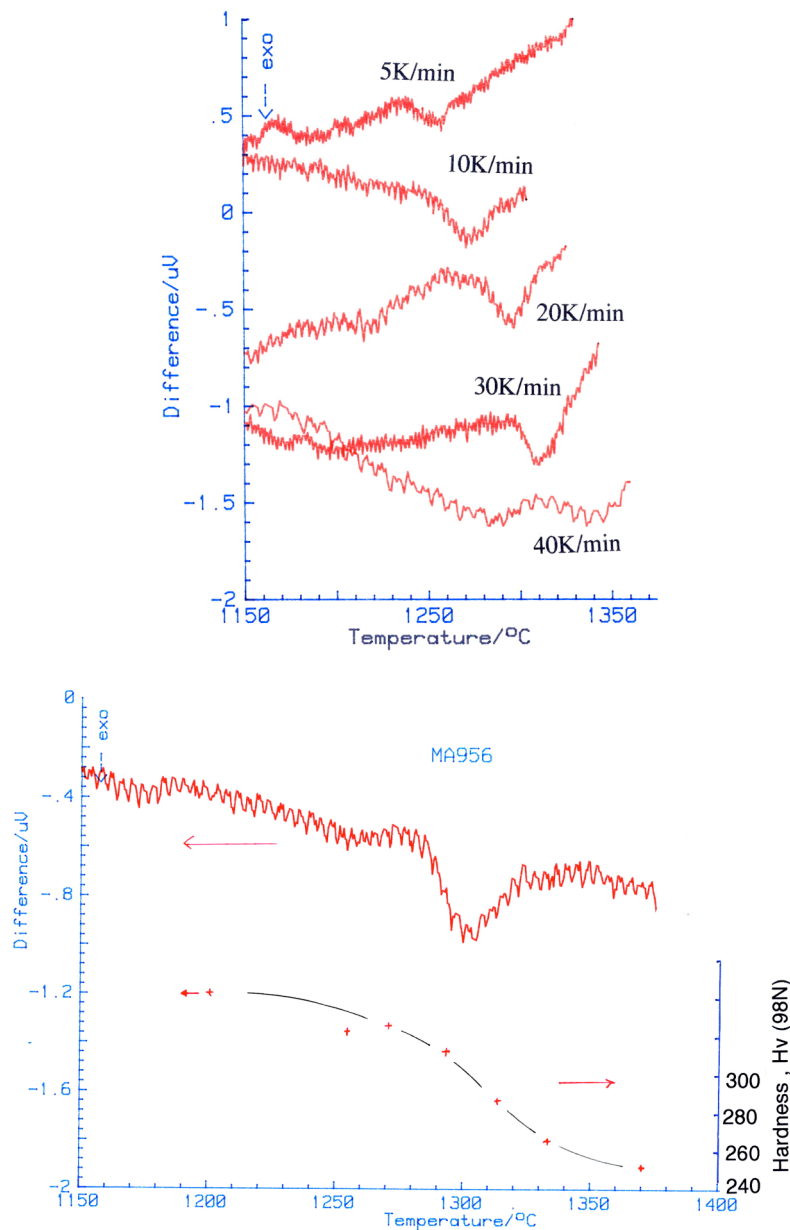


Fig. 2: (a) Superimposed DSC curves for MA956, obtained using a variety of heating rates. In all cases the reference was a recrystallised sample with almost the same mass as the sample, (b) A comparison between the DSC curve and hardness change during recrystallisation.

For MA956, the microstructure after processing, but prior to recrystallisation consists of extremely fine grains (mean linear intercept $L \approx 0.4 \mu\text{m}$) with large misorientations between the grains [9]. From the mean value of the stored energy release at the lowest heating rate

used ($\Delta H \approx 30 \text{ J mole}^{-1}$), the grain boundary energy per unit area (σ) can be estimated from the equation

$$\sigma = \Delta H L / 2V_M \quad (1)$$

where $V_M \approx 7.1 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$ is the molar volume of the alloy. Using this equation, the grain boundary energy is found to be about 0.8 J m^{-2} , indicating high-energy grain boundaries consistent with the large misorientations reported between the ultrafine grains in the extruded alloy [9]. The analysis assumes that most of the stored energy of the extruded sample is in the form of grain boundaries, with dislocations making a relatively small contribution which can therefore be neglected.

Theoretical Analysis

The phenomena noted above, *i.e.* the values of T_I , T_C and $T_C - T_I$, as a function of the heating rate, are expected intuitively. For example, it is natural that a thermally activated process occurring at a constant driving force, is retarded to higher temperatures if the heating rate is increased. It should therefore be possible to rationalise the observations using reaction rate theory.

In 1945, Holloman and Jaffe proposed that for a given isothermal heat treatment (at the absolute temperature T , time period t), the effectiveness B of that heat treatment should be related to the product $t \cdot \exp\{-Q/RT\}$, where Q is an activation energy, and R is the universal gas constant [10]. B is thus the integral of the curve of $\exp\{-Q/RT\}$ versus t . Hence, the time required to achieve the same metallurgical effect at another temperature can in principle be estimated by assuming that the product once evaluated, is constant for any other heat treatment. B is sometimes referred to as the kinetic strength of the heat treatment, and can easily be used to estimate the effectiveness of an anisothermal heat treatment. Alberry and co-workers [11,12] have used a similar procedure in the prediction of the grain size in steel welds, as have Ashby, Ion and Easterling [13-15]. The analysis has been usefully applied to the process of directional recrystallisation in a mechanically alloyed nickel-base superalloy (*MA6000*) by Baloch and Bhadeshia [16].

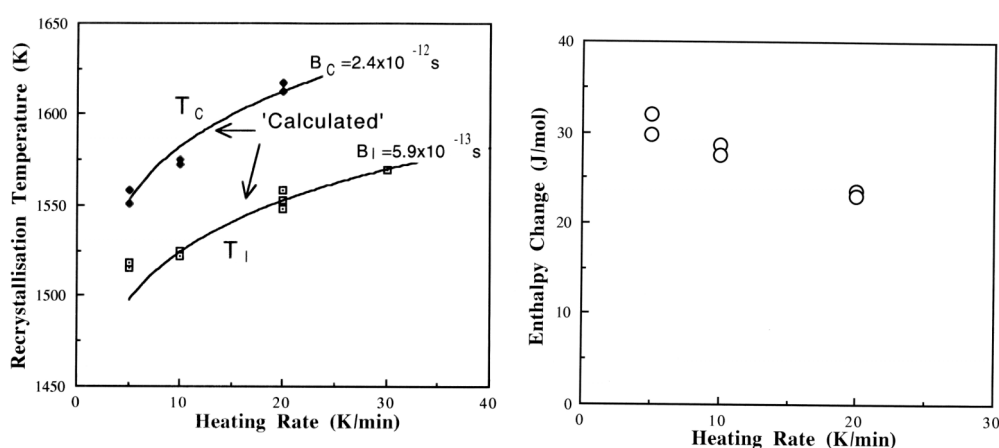


Fig. 3; (a) Plot of the observed values of T_I and T_C as a function of heating rate. The curves represent calculations to be discussed later in the text. (b) The enthalpy change (evolution of heat) due to recrystallisation, as a function of the heating rate.

For the present purposes, the kinetic strength approach requires knowledge of three quantities: the activation energy Q , and the critical values B_I and B_C of the kinetic strength for the initiation and completion (respectively) of directional recrystallisation. They were determined by fitting the DSC measurements to the equation

$$B = \int_{t=0}^{t_f} \exp\{-Q/RT\{t\}\} dt \quad (2)$$

where t_f represents the time at which the experiment is terminated. The notation $T\{t\}$ implies that the temperature is a function of time. The following values were determined experimentally: $Q = 470 \text{ kJ mole}^{-1}$, $B_I = 5.9 \times 10^{-13} \text{ s}$, $B_C = 2.4 \times 10^{-12} \text{ s}$. Figure 3 shows that the curves calculated using eq. 2 and these constants match the experimental data rather well over the entire range of heating rates. The theory is able to explain the key observations, that the recrystallisation process is retarded to higher temperatures, and that the temperature range over which recrystallisation occurs becomes larger, as the heating rate is increased.

The value of the activation energy appears to be rather large when compared with say the activation energy for self diffusion in iron $\approx 240 \text{ kJ mol}^{-1}$ [17]. This could indicate that the kinetic strength analysis is not a satisfactory theoretical representation of the physical processes involved in recrystallisation, in which case the activation energy must be regarded as an empirical constant. In *MA956*, the recrystallisation produces highly anisotropic grains parallel to the extrusion direction. Consequently, recrystallisation can be considered to be complete at any point along the extrusion direction when recrystallised grains touch along all directions normal to the extrusion direction. If the number of grains per unit area normal to the extrusion direction is N_A , then the time to complete isothermal recrystallisation at any point along the extrusion direction is given approximately by

$$t_C = 0.5(N_A)^{-0.5}v_N^{-1} \quad (3)$$

where v_N is the grain boundary velocity *normal* to the extrusion direction. The equation assumes that N_A does not vary with processing conditions, as is justified by the fact that the directionally recrystallised grain size does not vary much with heat-treatment. The grain boundary velocity can be represented as [18]

$$v_N = \delta\nu \exp\{-Q/RT\}[1 - \exp\{-\Delta G/RT\}] \quad (4)$$

where δ and ν are the distance and atomic jump frequency across the boundary respectively, and ΔG is the effective driving force for recrystallisation (it does not vary with T). It follows that

$$t_C \exp\{-Q/RT\} = (2\delta\nu N_A^{0.5}[1 - \exp\{-\Delta G/RT\}])^{-1} \quad (5)$$

The driving force ΔG for recrystallisation does not vary with temperature. It is given approximately by $\Delta G \approx \Delta G_s - (C_I V_V V_M \sigma/r)$, where ΔG is the stored free energy in the material, r is the radius of grain boundary pinning particles, V_V is the volume fraction of pinning particles, σ is the grain boundary energy per unit area, and V_M is the molar volume. C is a constant whose magnitude depends on the details of the pinning process [20]. Thus, ΔG . (which is approximately $\Delta H = 30 \text{ J mole}^{-1}$) represents an upper limit to ΔG , and it is easily demonstrated that the term in square brackets in eq. 5 is insensitive to temperature. It

follows that the left hand side of equation 5 is exactly equivalent to the equation used in the kinetic strength analysis. This can be taken to give a physical basis to the kinetic strength analysis, so that Q can now be interpreted to represent the activation energy for the migration of grain boundaries in a direction normal to the extrusion direction of *MA956*. It remains to be established whether the activation energy for migration parallel to the extrusion direction is much smaller, as might be indicated by the larger growth velocity along that direction. Recent work [9] has demonstrated that there is a highly anisotropic distribution of yttrium oxide particles in *MA956*, the particles being aligned parallel to the extrusion direction. This might be responsible for the abnormally large value of Q , although how such alignment can influence the activation energy, and other matters relating to the derivation of t_C , require further investigation.

The analysis presented above is consistent with our metallographic observations (Figure 4). During continuous heating, the recrystallised grains grow rapidly along the extrusion direction, and the sidewise coalescence of these grains is found to occur at a much slower rate.

TMO-2

There has been considerable research to discover how directional recrystallisation is triggered in mechanically alloyed ODS steels and nickel-base alloys. It has been suggested in the past that in the nickel-base alloys, the onset of recrystallisation coincides with the dissolution of γ' precipitates, but recent work has indicated that the "recrystallisation temperature" can actually be higher than that at which γ' dissolves [7,8]. It has been speculated that directional recrystallisation might be initiated when the grain boundary mobility suddenly rises because grain boundary solute drag effects are overcome at elevated temperatures [19], but this can only be established by making direct measurements of the grain boundary composition. A simpler explanation, consistent with both the steels and the superalloys, is that recrystallisation occurs when the kinetic strength achieves the required value. This means essentially that the heat treatment must provide enough thermal energy to induce recrystallisation. We present here some initial data on alloy *TMO-2*, which is an ODS nickel-base superalloy. Figure 5 shows that the γ' solution temperature is far below that at which directional recrystallisation occurs, the difference being more than 100 °C. This result confirms that the recrystallisation process is not essentially connected with the solution of γ' precipitates.

CONCLUSIONS

It appears that the kinetic strength analysis is capable of rationalising the directional recrystallisation behaviour of mechanically alloyed, yttrium oxide-dispersion strengthened steel *MA956*. It is possible to understand the fact that the recrystallisation process is shifted to higher temperatures as the heating rate is increased. The increase in the temperature range over which recrystallisation occurs is also predicted.

The parameters used in the kinetic strength analysis must, however, be investigated further using models which better represent the physical processes inherent in recrystallisation. Further theoretical work is needed to model the directional recrystallisation process, so that factors such as the activation energy can be convincingly interpreted on the basis of firm physical principles. The enthalpy change accompanying the recrystallisation of *MA956* can be attributed largely to the energy stored in the high-misorientation boundaries between the ultrafine grains in the unheat-treated condition of *MA956*.

For the nickel-base alloy *TMO-2*, calorimetric analysis demonstrates that directional recrystallisation occurs at a much higher temperature when compared with γ' dissolution.

This confirms that γ' dissolution has little to do with the onset of directional recrystallisation in nickel-base, mechanically alloyed, ODS superalloys.

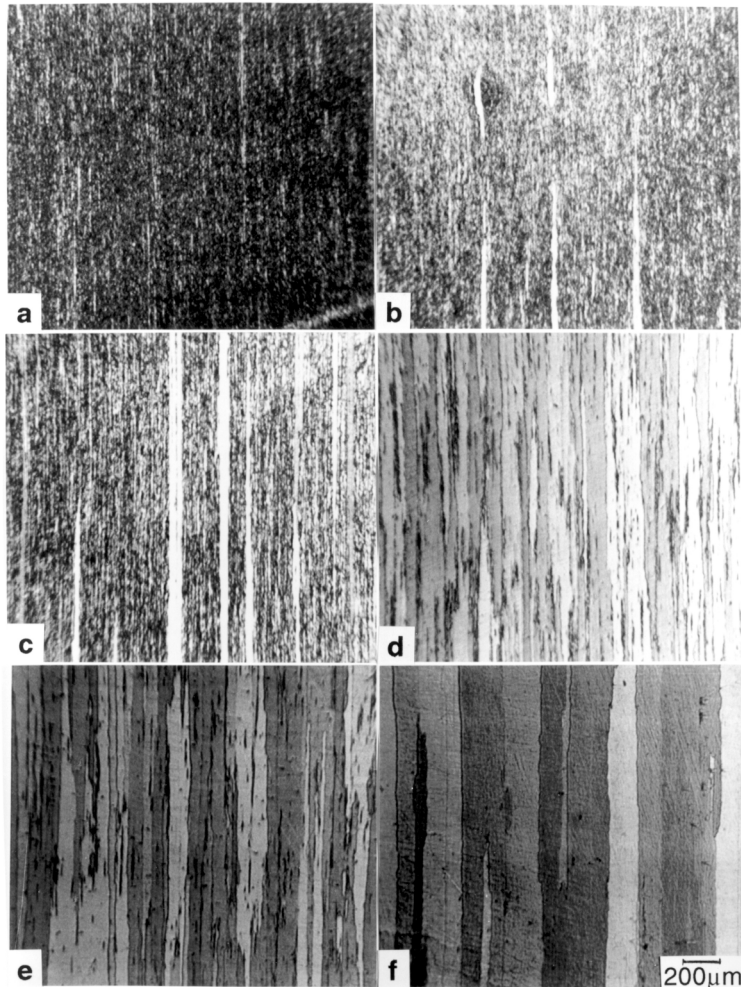


Fig. 4: Microstructural evolution in *MA956* during heating at 20 Kmin^{-1} . The extrusion direction is vertical, (a, c) Early stages of recrystallisation, heated to 1526 K, HV 322. (b, d) Partially recrystallised, heated to 1565 K, HV 312. (e) Advanced stage of recrystallisation, heated to 1585 K, HV 288. (f) Fully recrystallised, heated to 1643 K, HV 253.

ACKNOWLEDGMENTS

We are grateful to Professor C. J. Humphreys (University of Cambridge) for the provision of laboratory facilities. The work was carried out under the auspices of the "Atomic Arrangements: Design and Control" project, which is a collaborative venture between the Research and Development Corporation of Japan and the University of Cambridge. The steel and superalloy samples were kindly provided by INCO Alloys Ltd. (U. K.) and IHI (Japan), respectively.

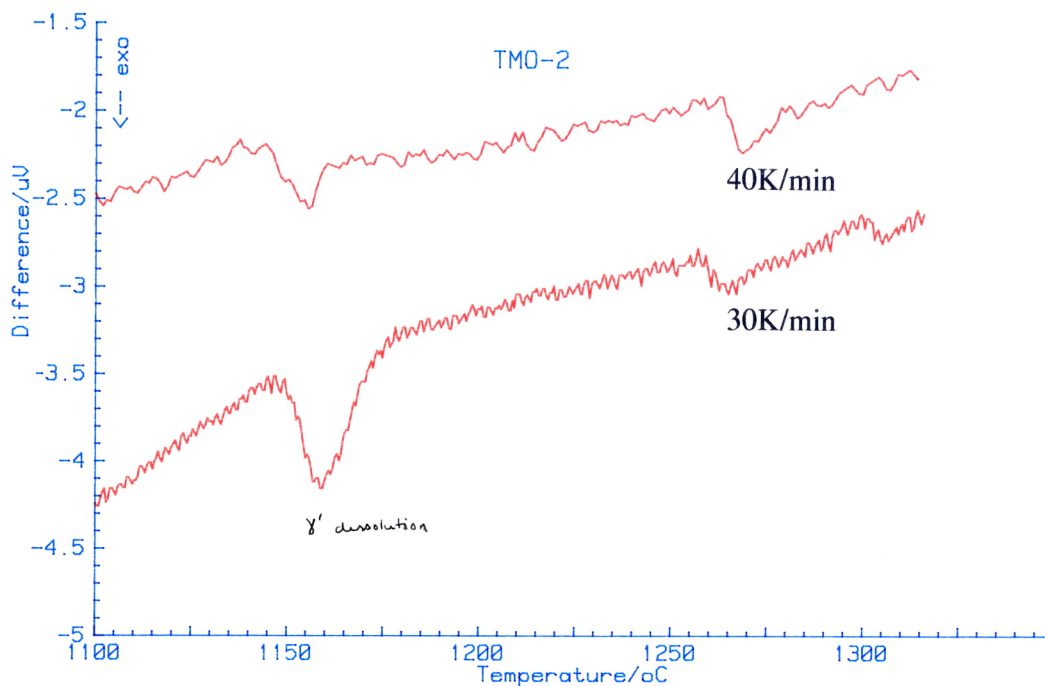


Fig. 5: DSC curves for *TMO-2*, using a recrystallised reference of a mass similar to the sample, (a) Heating rate 30 K min⁻¹. (b) Heating rate 40 K min⁻¹.

REFERENCES

- 1) Benjamin, J. S.; Metall. Trans., 1970, 1, 2943
- 2) Hack, G. A. J.: Powder Metallurgy, 1984, 27, 73
- 3) Vandermculen, W. and Coheur, L.: Powder Metallurgy, 1981, 3, 141
- 4) Huet, J. J, Wilde, L. De. and Leroy, V.: Metallurgie, 1979, XIX, 37
- 5) Cairns, R. L., Curwick, L. R. and Benjamin, J. S.: Metall. Trans. A, 1975, 6A, 179
- 6) Singer, R. F. and Gessinger, G. H.: Metall. Trans. A, 1982, 13A, 1463
- 7) Mino, K., Nagakawa, Y. G. and Ohtomo, A.: Metall. Trans. A, 1987, 18A, 777
- 8) Kusunoki, K., Sumino, K., Kawasaki, Y., Yamaaaki, M.: Metall. Trans. A, 1990, 21A, 547
- 9) Baloch, M.: Ph.D. Thesis, University of Cambridge, , 1989
- 10) Holloman, J. H. and Jaffe, L. D.: Trans. AIME, 1945, 162, 223
- 11) Alberry, P. J. and Jones, W. K. C.: Metals Technology, 1977, 4, 557
- 12) Alberry, P. J., Brunnstrom, R. R. L. and Jones, K. E.: Metals Technology, 1983, 10, 28
- 13) Ashby, M. F. and Easteriing, K. E.: Acta Metall., 1982, 30, 1969
- 14) Ion, J. C., Easteriing, K. E. and Ashby, M. F.: Acta Metall., 1984, 32, 1949
- 15) Ashby, M. F.: Proc. R. Soc., 1987, A322, 393
- 16) Baloch, M. and Bhadeshia, H. K. D. H.; Materials Science & Technology, 1990, 6, 1236
- 17) Fridberg, J, Torndahl, L.-E. and Hillert, M.: Jernkontorets Ann., 1969, 153, 263
- 18) Christian, J. W.: Theory of Transformations in Metals and Alloys, Part I, 2nd Edition, Pergamon Press, Oxford, 1975, , 478
- 19) Jongenburger, P.: Thesis no. 773, Ecole Polytechnique Federale de Lausanne, Switzerland, 1988
- 20) Zener, C.: Private communication to C. S. Smith, Trans. Met. Soc. A. I. M. E., 1949, 175, 15

