Grain control in mechanically alloyed oxide dispersion strengthened MA 957 steel

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Mechanically alloyed oxide dispersion strengthened stainless steels tend to recrystallise into columnar grains, a microstructure ideal for certain creep applications. In other circumstances, equiaxed grain structures are desired. In this paper, two methods are described which have been developed to ensure the reproducible development of equiaxed or refined grain microstructures in an alloy, MA957, which has previously not been amenable to control. Grain refinement has been achieved by controlling the stored energy, so that grain boundary velocities are reduced to a level which allows nucleation to develop at many sites, and by inducing a phase transformation from ferrite to austenite. MST/1779

Introduction

Oxide dispersion strengthened alloys produced using a mechanical alloying technique have the potential for higher creep resistance and stability at elevated temperatures, compared with conventional alloys.[1-6] In the mechanical alloying process, metallic powders or intermetallic compounds are induced to form a solid solution by means of intense deformation. There are two major commercial variants of mechanical alloy: the nickel based alloys intended for aerospace applications,[6,7] and those based on ferritic iron with potential applications at somewhat lower temperatures. The density of the ferritic alloys is about 10% lower than that of the nickel base alloys, providing a significant strength/weight advantage, and a lower thermal expansion coefficient, which is beneficial when thermal fatigue is an important design criterion.[8] In nuclear reactor applications, the ferritic structure is more resistant to neutron damage.[9] A mechanically alloyed ferritic stainless steel Incoloy MA 957 has been developed as a nuclear fuel cladding material for fast breeder reactors.[10]

After mechanical alloying and processing into bulk form, MA 957 has an ultrafine microstructure containing submicrometre sized grains of ferrite. The hardness in this condition is unacceptably high, so the alloy is used in the recrystallised condition. Recrystallisation can be carried out isothermally, in a temperature gradient, or using zone annealing. All these heat treatments result in a coarse columnar grain structure akin to a directionally solidified microstructure. The reason for the persistent recrystallisation into a columnar rather than an equiaxed grain structure is that the alloy contains a dispersion of oxide particles which are aligned along the extrusion direction,[11] so the easiest grain growth path is along that direction.

A columnar (or directionally recrystallised) grain structure is ideal for elevated temperature applications where creep resistance is important. However, when the alloy is in tubular form, its resistance to hoop stresses is found to be less than desirable. Different metal working conditions can influence the degree of anisotropy,[12,13] but it has not yet been possible to produce an equiaxed microstructure in the range 20–40 μm. The major aim of the present work was to develop heat treatments capable of causing recrystallisation into equiaxed grains, even though the initial microstructure contains a highly anisotropic dispersion of oxide particles. The method used involves the control of stored energy before recrystallisation and exploits a recently discovered phase transformation in MA 957.

Experimental procedure

The chemical composition of the alloy used is given in Table 1. The alloy was supplied in an unrecrystallised condition. It was fabricated by charging a water cooled vertical attritor with three primary powders (elemental iron, prealloyed metallic alloys, and yttria) for mechanical alloying. Consolidation of the resultant powder was achieved by extrusion at 1000°C with the alloy packed in a mild steel can. This was followed by rolling at 1000°C, with a reduction in diameter from 54 to 9·5 mm. Although the extrusion and rolling are carried out at relatively high temperatures, they cannot be classified here as 'hot working' processes, since the final microstructure represents a cold deformed condition with submicrometre sized elongated and heavily dislocated ferrite grains.[11]

The stored energy before recrystallisation was controlled by 'preannealing' at a temperature high enough to permit recovery but not recrystallisation. Thus, preannealing was carried out at 1150°C before heating to 1350°C to induce recrystallisation.

Square sectioned specimens of dimensions $3 \times 3 \times 20$ mm were cut from the as extruded rod. The heat treatments were carried out in a conventional resistance furnace, the samples being protected by sealing in quartz tubes filled with a partial pressure of pure argon.

Optical microscopy was used to observe the microstructures of both as received and heat treated specimens. The etchant used was 2 g $CuCl_2$, 40 ml HCl, and 40–80 ml ethanol. Transmission electron microscopy (TEM) was carried out using a Philips EM 400 microscope operated at 120 kV. Thin foils were prepared using a Fischione twin jet electropolisher with 5% perchloric acid, 25% glycerol, and ethanol mixture. The polishing voltage used was about 55 V.
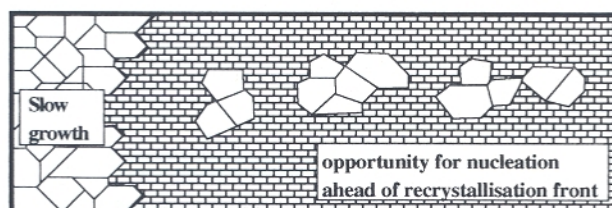
Differential scanning calorimetry (DSC) was carried out using a Netzsch DSC 404/3/413/D, which is a specially designed high temperature, heat flux DSC with computer control and data acquisition. It uses a platinum–rhodium furnace which has very low temperature gradient characteristics. The sample and reference are placed in thermally balanced platinum crucibles. A differential signal is generated when an event causes a difference in heat evolution or heat capacity between the sample and its reference; this signal can be converted into thermodynamic data associated with the event. Experiments can be carried out to a maximum temperature of about 1500°C.

Calorimetric measurements were carried out during continuous heating (10 K min^{-1}); both the sample mass

(a) High stored energy, high anisotropic growth velocity
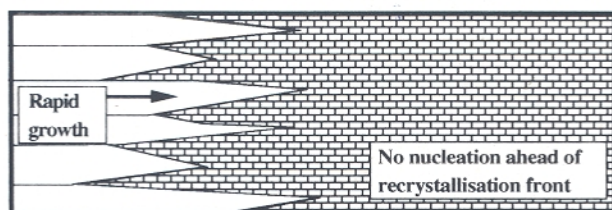
(b) Low stored energy, low anisotropic growth velocity

1 Schematic development of recrystallisation process for *a* high and *b* low stored energy

2 Vickers hardness data for preannealed samples and for samples subsequently recrystallised by heating to 1350°C

and reference mass were typically ~ 200 mg. The reference was made of the same alloy as the sample, but it was in the recrystallised state. All the experiments were carried out using an argon atmosphere in the DSC chamber, the argon flowrate being 50 cm^3 min^{-1}.

Thermodynamic phase stability calculations were carried out using the Mtdata package from the National Physical Laboratory.[14]

Preannealing experiments

It is emphasised above that MA 957 tends to recrystallise into coarse columnar grains parallel to the extrusion/rolling direction, i.e. the alloy directionally recrystallises. This is irrespective of whether the heat treatment is carried out with the sample in a temperature gradient, whether the sample is zone annealed (i.e. a moving hot zone traverses the length of the sample), or whether the sample is isothermally annealed. Indeed, the grains always tend to grow along the extrusion direction, even when the temperature gradient is orientated normal to the extrusion direction.[11] For all heat treatments, a jagged recrystallisation front develops and propagates along the length of the sample, presumably because the 'nucleation' occurs at the sample surfaces.

It follows that, unlike for some other alloys, the reason why recrystallisation is directional has little to do with the existence of any temperature gradients during annealing. It has been revealed using TEM that the distribution of yttria particles is not uniform;[11] the particles tend to align parallel to the extrusion direction. Consequently, the grain boundary velocity is anisotropic, being highest along the extrusion direction. This explains the development of the directional microstructure.

The particle dispersions are therefore not strong enough to pin grain boundaries; they simply hinder grain boundary motion, to varying degrees along different directions. In
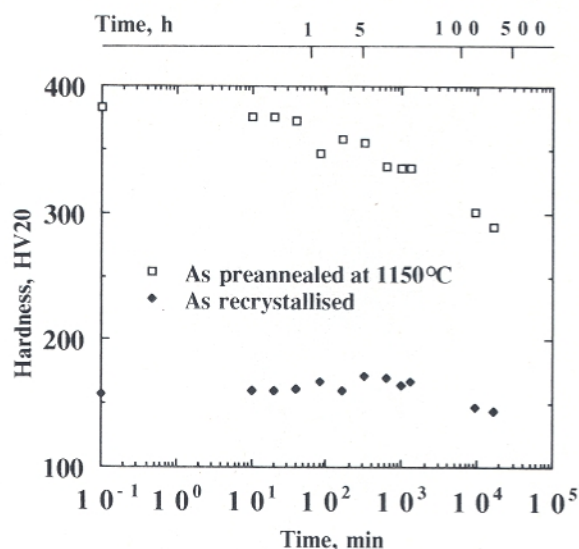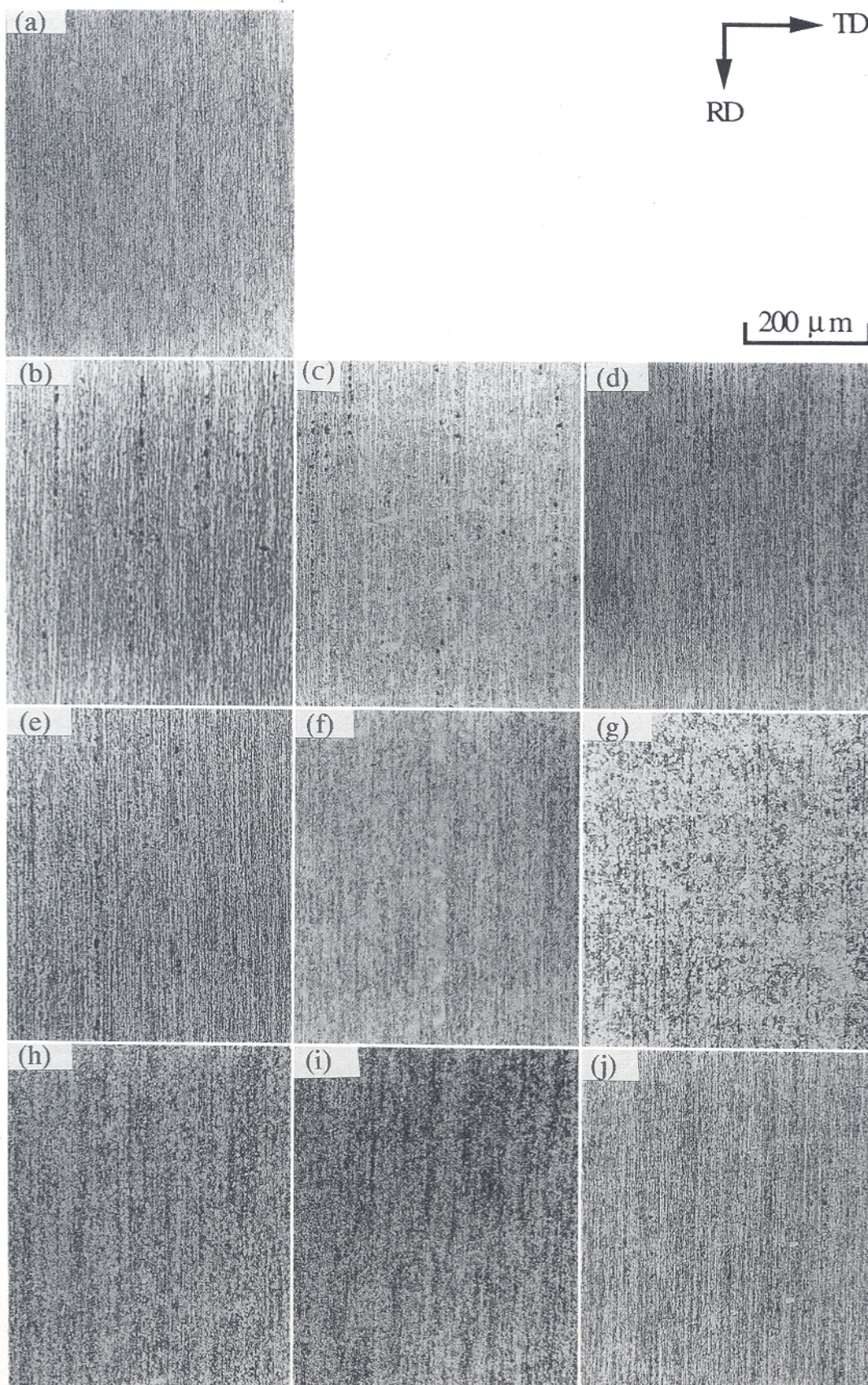
fact, the mechanical alloying and extrusion process results in a cold worked microstructure with an ultrafine, sub-micrometre sized grain structure which is very hard. Most of the stored energy of the alloy is thus in the form of grain boundaries. This stored energy is so large that moving grain boundaries can easily overcome the drag from the particle dispersion.

To summarise, the directionally recrystallised microstructure is anisotropic because the growth velocity is much higher along the extrusion direction. Once initiated at the sample surfaces, the recrystallisation front propagates so rapidly that there is no opportunity for recrystallisation to develop from other locations in the sample (Fig. 1a). The grain intercept along the transverse direction tends to be insensitive to the heat treatment, probably being controlled by the number of initial sites at which recrystallisation can commence. Thus, a more isotropic grain structure could in principle be produced by reducing the grain velocity along the longitudinal direction (Fig. 1b). This can be achieved by reducing the stored energy, via some recovery process before recrystallisation.

Recrystallisation in MA 957 tends to occur at temperatures in excess of 1300°C, so a set of preannealing experiments was designed to dissipate some of the stored energy. This involved prolonged annealing at 1150°C before heating to 1350°C to induce recrystallisation.

Although the hardness decreases slightly during preannealing at 1150°C for 10 min–80 h (Fig. 2), optical micrographs reveal no obvious structural changes (*see* Fig. 3). This is consistent with recovery effects occurring during the preannealing process. Subsequent recrystallisation at 1350°C in some cases produced equiaxed grain microstructures (Fig. 4), but the results were erratic. Such behaviour is a reflection of the fact that mechanical alloying is a difficult process, the alloys being somewhat inhomogeneous. Indeed, an attempt to reproduce the equiaxed microstructure shown in Fig. 4 failed, as shown in Fig. 5. However, preannealing for 160 h at 1150°C gave a reproducible equiaxed, fine grained microstructure, irrespective of the position of the sample within the extruded bar, as shown in Figs. 6a and 6b. This is because in all positions the stored energy (and hence the growth velocity) has been reduced sufficiently to give the transition from a directionally recrystallised to an equiaxed microstructure.

Consistent with this, further preannealing (280 h at 1150°C) resulted in a deterioration of the microstructure,

Table 1 Chemical composition of MA 957 alloy, wt-%

C	Cr	Mo	Ti	Y$_2$O$_3$	Fe
0·01	14·0	0·3	1·0	0·27	Bal.

Supplied by Inco Alloys (Hereford).

a as extruded; after isothermal annealing at 1150°C for *b* 10, *c* 20, *d* 40, *e* 80, *f* 160, *g* 320, *h* 640, *i* 960, *j* 1280 min

3 Optical microstructures of as extruded and preannealed MA 957 samples: no obvious structural changes can be seen
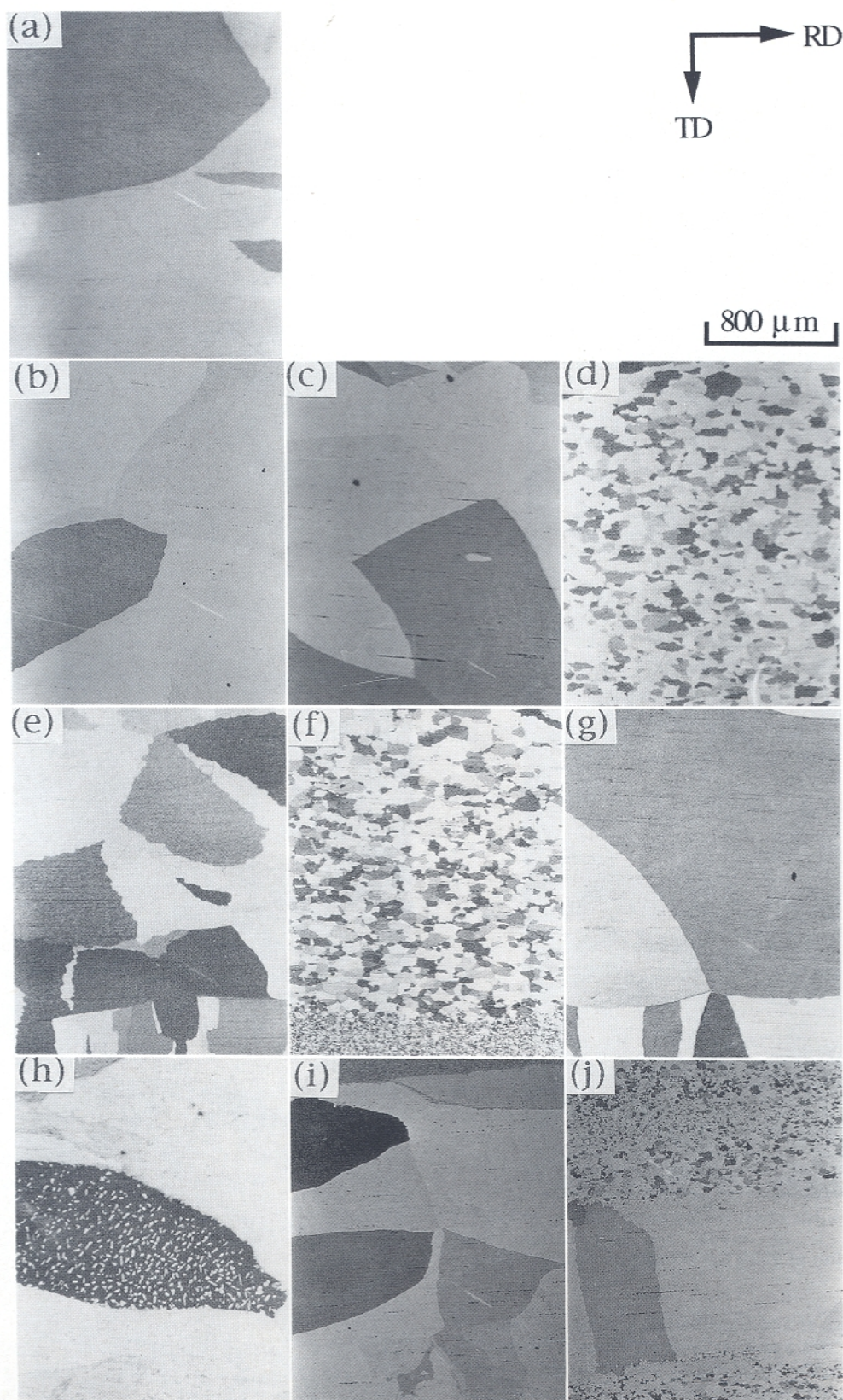
a without preannealing; preannealed at 1150°C for *b* 10, *c* 20, *d* 40, *e* 80, *f* 160, *g* 320, *h* 640, *i* 960, *j* 1280 min
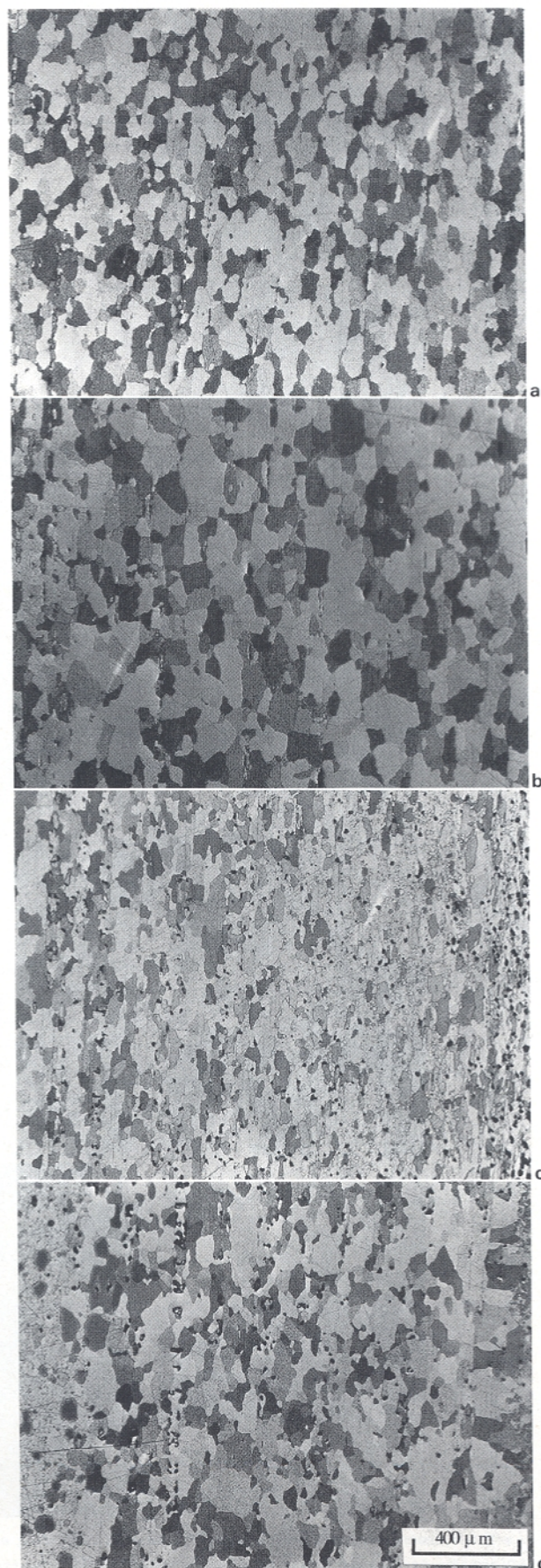
4   Microstructures of preannealed samples of Fig. 3 after subsequent recrystallisation at 1350°C for 1 h (optical micrographs)

TD

RD

800 μm
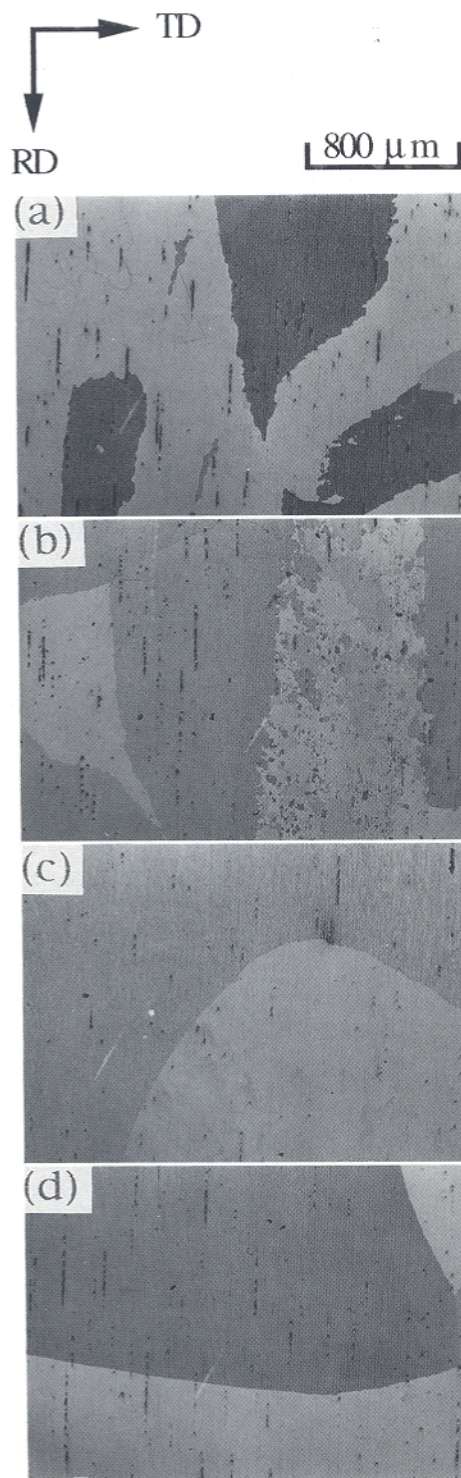
5   **Microstructures obtained by preannealing at 1150°C for** *a* **160,** *b* **320,** *c* **640, and** *d* **1280 min, then recrystallising at 1350°C/1 h (optical micrographs)**

as shown in Figs. 6c and 6d. Although equiaxed grains were obtained, their size was finer, and varied as a function of position. Clearly, the stored energy had decreased to a level where the grain size begins to be limited by Zener pinning, as the pinning force becomes comparable to the driving force for grain boundary migration. The microstructure thus becomes sensitive to any inhomogeneous distribution of particles.

This theory is summarised in Fig. 7. When the driving force for recrystallisation is very large, a directional grain structure is obtained because the growth rate in the
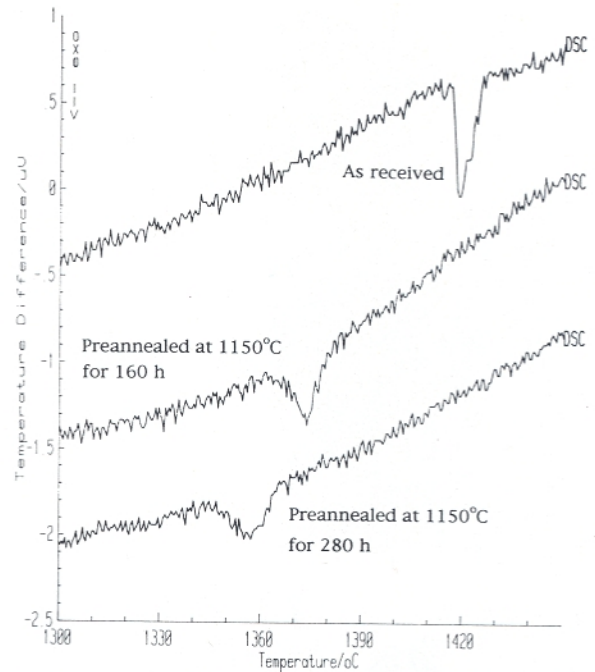

400 μm

6   **Microstructures of samples preannealed at 1150°C for** *a, b* **160 h and** *c, d* **280 h, then recrystallised at 1350°C for** *a, c* **20 and** *b,* d **40 min (optical micrographs)**
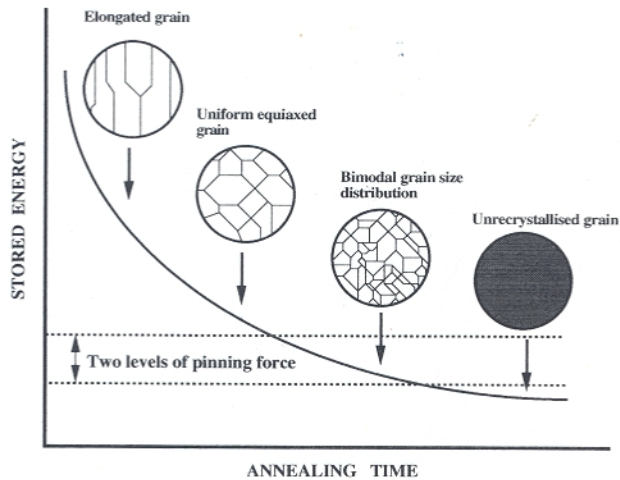
7 Schematic diagram of role of stored energy in determining final microstructure of alloy preannealed, then recrystallised: two levels of pinning force emphasise that mechanically alloyed steel contains inhomogeneous distribution of particles

9 DSC curves of alloy in as received condition and as preannealed at 1150°C for 160 and 280 h (heating rate 5 K min⁻¹)

longitudinal direction is large (relative to the pinning force), so there is no opportunity for recrystallisation to develop at sites other than that of initial nucleation. This does not apply at intermediate levels of stored energy and almost uniform equiaxed grain structures are obtained. When the driving force for recrystallisation becomes comparable to the pinning force, there is not only a refinement in the microstructure, but also a heterogeneous grain size reflecting variations in the oxide dispersions within the alloy.

The effect of preannealing on the stored energy and microstructure was confirmed further using TEM and DSC. Figure 8 shows the effect of preannealing on the annihilation of dislocations in the deformed material; it can be seen that there is a reduction in the dislocation density during the preannealing heat treatment (1150°C for 160 h). The stored energy decreases correspondingly from 1·0 (as received) to 0·7 (as preannealed at 1150°C for 160 h) to 0·5 J g⁻¹ (as preannealed at 1150°C for 280 h). (The DSC curves are shown in Fig. 9).

Refinement by transformation

Alloy MA 957 is essentially an Fe–Cr alloy which is designed to be a ferritic stainless steel. Alloys such as these rely on the 'γ loop' on the phase diagram: beyond a certain limiting concentration of chromium, the alloy becomes ferritic up to the melting temperature, whereas below that concentration, there is a range of temperatures over which austenite can also form. It has recently been reported that MA 957 lies just within the γ loop, so a small amount of austenite can be generated by heat treatment in the range 970–1010°C.[15] The occurrence of austenite phase in this steel was established using thermodynamic phase stability calculations and confirmed using metallography. The details
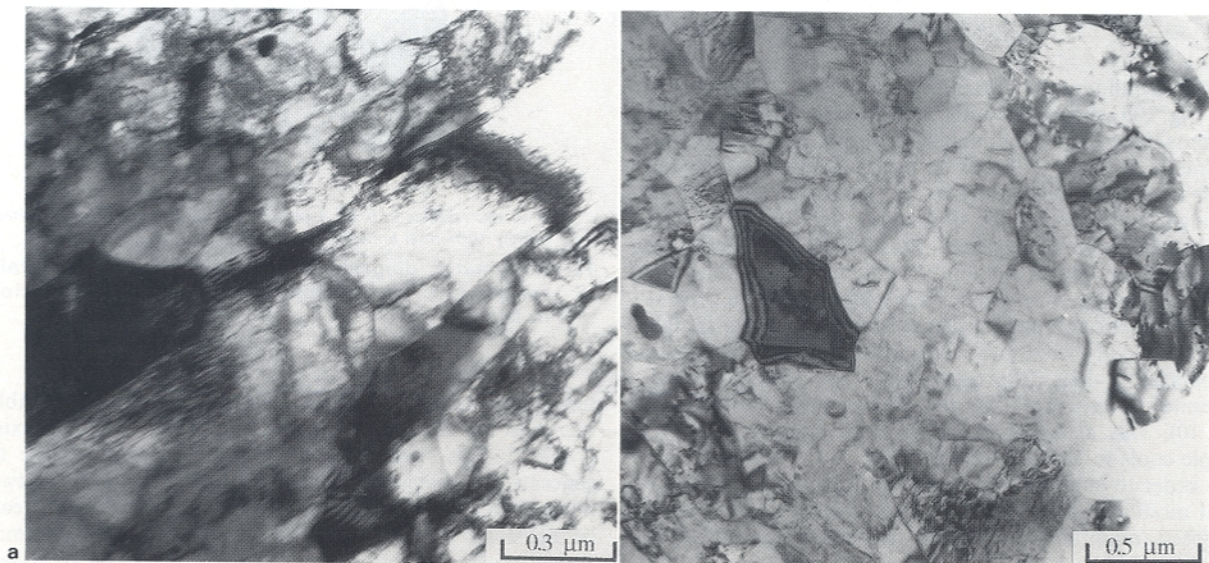
8 Microstructure of alloy in *a* as received condition and *b* as preannealed at 1150°C for 160 h (TEM): low dislocation density in as preannealed steel indicates release of stored energy after recovery annealing
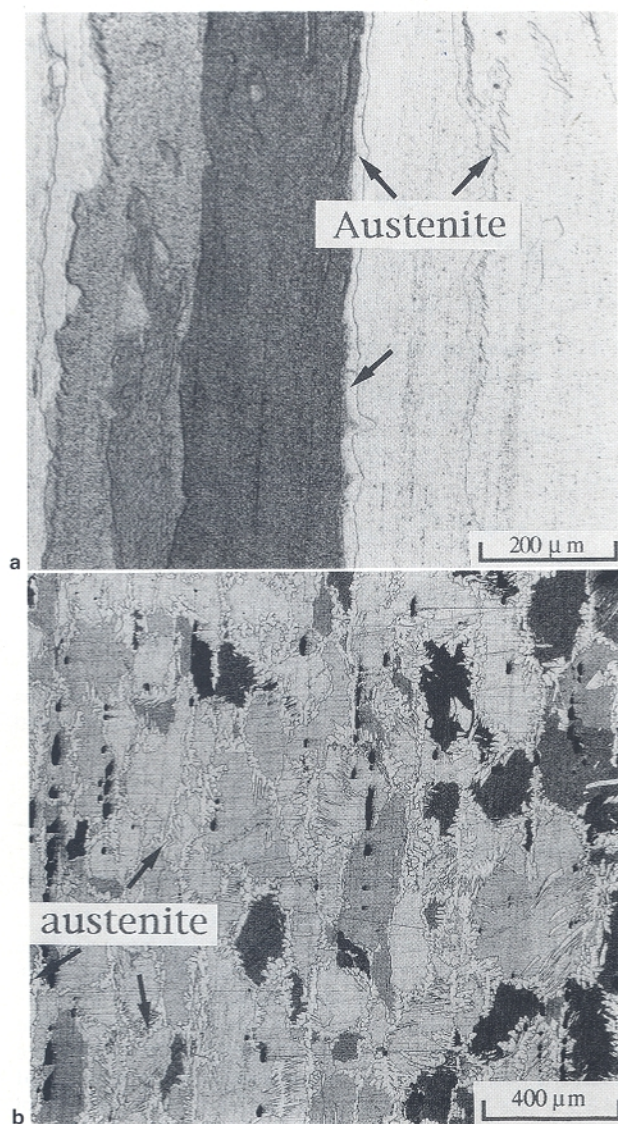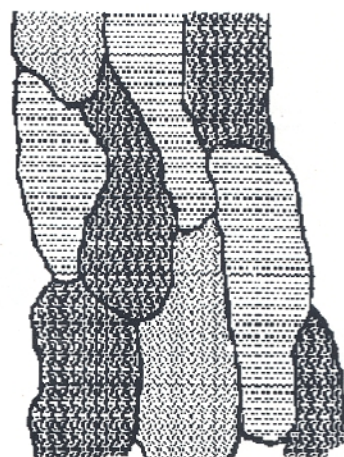
a isothermal heat treatment at 1000°C for 24 h; b air cooling from 1350°C

10 Allotriomorphic and Widmanstätten austenite obtained at ferrite grain boundaries during air cooling of sample from recrystallisation temperature (optical micrographs)

a as recrystallised; b as a plus ferrite and austenite two phase region isothermal annealing; c as b followed by air cooling

11 Schematic diagram showing sequence of grain refinement via austenitic phase transformation in MA 957

of the metallography have been published elsewhere,[15] but Fig. 10a shows the austenite layers formed at the columnar ferrite grain boundaries during isothermal heat treatment at 1000°C for 24 h. Both allotriomorphic and Widmanstätten austenite can be generated during air cooling from 1350°C as the alloy 'clips' the γ loop (Fig. 10b).

The generation of austenite phase thus can provide an alternative method of refining the microstructure after the extruded sample has been recrystallised into a coarse grained directional microstructure at 1350°C. If the sample is cooled slowly from the recrystallisation heat treatment temperature, then allotriomorphic or Widmanstätten austenite is generated at the ferrite grain boundaries (Fig. 10). This austenite decomposes to martensite as the sample cools to ambient temperature.
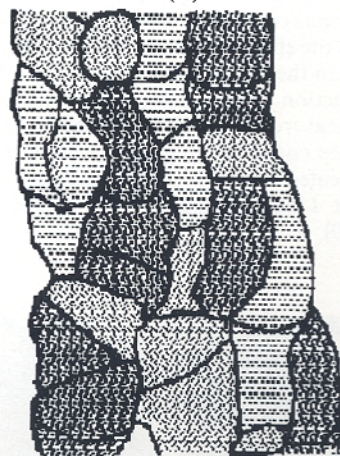
In order to enhance the growth of the austenite phase, a small modification of the basic composition of MA 957 is proposed, maintaining the high chromium concentration necessary for oxidation and corrosion resistance. Thermodynamic phase stability calculations suggest that an addition of only 0·5 wt-%Ni increases the temperature range over which the austenite is stable and considerably increases the maximum amount of austenite that can exist (Table 2). This should make the alloy more amenable to generate the austenite phase when heat treated in the two phase field. Therefore, the grain refinement of MA 957 can be achieved by recrystallising the steel then isothermal annealing in the two phase field (Fig. 11). The modified alloy is to be manufactured by Inco Alloys for confirmatory experiments which will be reported when completed.

Table 2 Thermodynamic phase stability calculations for MA 957 with addition of 0·5 wt-%Ni: concentrations and phase fractions are given in wt-% and bcc and fcc forms of iron are designated α and γ respectively

Temperature, °C	α	γ	C_α	C_γ	Cr_α	Cr_γ	Mo_α	Mo_γ	Ni_α	Ni_γ
830	100	...	0·010	...	14·00	...	0·300	...	0·500	...
870	80·8	19·2	0·007	0·024	14·39	12·36	0·309	0·261	0·426	0·813
910	61·8	38·2	0·005	0·018	14·88	12·57	0·321	0·266	0·379	0·695
950	54·3	45·7	0·005	0·016	15·13	12·66	0·326	0·269	0·371	0·653
990	55·5	44·5	0·005	0·016	15·11	12·62	0·326	0·268	0·382	0·647
1030	63·5	36·5	0·006	0·022	14·89	12·45	0·321	0·264	0·407	0·663
1070	77·0	23·0	0·006	0·022	14·53	12·21	0·312	0·258	0·442	0·694
1110	94·3	5·7	0·009	0·030	14·12	11·94	0·303	0·252	0·486	0·735
1150	100	...	0·010	...	14·00	...	0·300	...	0·500	...

Summary

A reduction in the stored energy of MA 957 to an optimum value permits the recrystallisation process to generate a uniform, equiaxed grain structure with a grain size in the range consistent with the achievement of more isotropic mechanical properties. This is in spite of the non-homogeneous dispersion of oxide particles.

Alternatively, grain refinement may be achieved by inducing the formation of austenite over an intermediate temperature range, the austenite decomposing to martensite on cooling to ambient temperature. A thermodynamic analysis has indicated that a small change in the chemical composition (the addition of 0·5 wt-%Ni) could facilitate formation of austenite. Further work is required to verify the mechanical properties of the new microstructures.

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