Atomic Structure of Mechanically Alloyed Steels

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ABSTRACT

The process of mechanical alloying involves the formation of solid solutions by the intense deformation of mixtures of different powders. It can therefore force atoms into positions where they may not prefer to be under equilibrium conditions. In this work we investigate the atomic structure of two mechanically alloyed steels with the commercial designations *MA956* and *MA957*. They were both studied in the unrecrystallised state using the technique of field-ion microscopy and atom probe analysis, which permits the determination of both microstructure and chemistry with an atomic resolution.

It is found that there is a very fine dislocation cell structure (on the scale of about 30 nm) in the alloys prior to recrystallisation heat treatments. This is consistent with our earlier microstructural and thermodynamic data that the alloys are in a cold-deformed state after mechanical alloying, extrusion and/or hot-rolling. This is in contrast to the mechanically alloyed nickel base ,superalloys which have consistently been found to be in a primary recrystallised state following extrusion.

Analysis of atom-by-atom data suggests that the solid solutions of *MA956* and *MA957* are random in that the pair probabilities can be calculated simply from the alloy chemistry. This is unexpected, since thermodynamic data indicate that, for example, the iron and chromium atoms prefer to be in the vicinity of like atoms. It is concluded that the randomness of the solid solution is a direct consequence of the mechanical alloying process.

THE SYNTHESIS OF MATERIALS by high energy ball milling of powders, termed mechanical alloying, was first developed by Benjamin et al. [1] to provide complex oxide dispersion strengthened alloys for high temperature applications. There have been many studies on the recrystallisation behaviour of mechanically alloying metals during the past two decades. However, the atomic structure of the mechanically alloyed solid solutions do not appear to have been examined in detail. Given the nature of the mechanical alloying process, it is possible that the distribution of atoms is likely to be in a nonequilibrium state.

The intense deformation associated with mechanical alloying can force atoms into positions where they may not prefer to be when at equilibrium. The purpose of the present work was to investigate this atomic structure of solid solutions formed by the mechanical alloying process.

EXPERIMENTAL PROCEDURE

Samples with dimensions $0.35 \times 0.35 \times 20$ mm were machined from the mechanically alloyed steels *MA956* and *MA957*, whose chemical compositions are given in Table 1. The alloys were prepared at INCO (Hereford) using mechanically alloyed' powder which was consolidated by hot extrusion followed by hot rolling. This gives the cold-worked microstructure illustrated in Fig. 1, with an ultrafine submicron grain size. The samples were studied in this as-received condition, without the usual heat treatment which leads to recrystallisation into a coarse and highly anisotropic columnar grain structure.

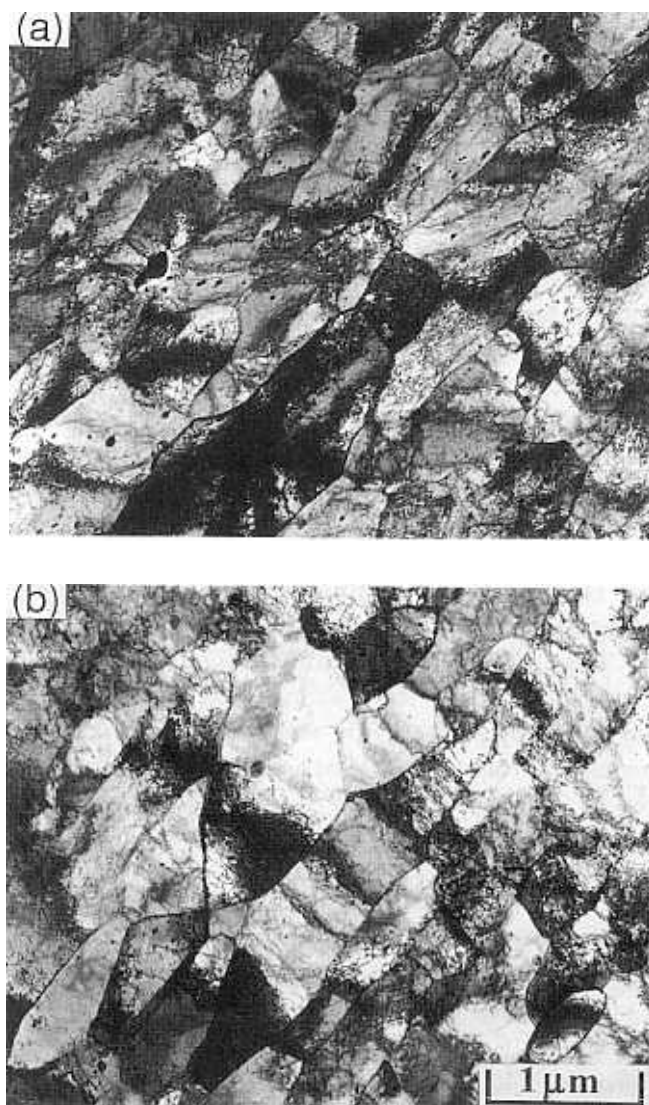| Alloy	C	Cr	Al	Ti	Mo	Y_2O_3
MA956 wt.%	0.01	20.0	4.5	0.5	–	0.50
MA956 at.%	0.044	20.2	8.8	0.55	–	
MA957 wt.%	0.01	14.0	–	1.0	0.3	0.27
MA957 at.%	0.046	14.9	–	1.15	0.17	

Table 1 Chemical compositions. The atom percent data exclude the yttrium oxide

Figure 1. Transmission electron micrographs taken from longitudinal sections of alloys (a) MA956 and (b) MA957. The samples are in the as–received condition, identical to those used for field ion microscopy.

A two–stage electropolishing technique was used to prepare fine tips for field ion microscopy. The electropolishing solutions were 25% perchloric acid, 25% glycerol, and 70% ethanol for the first stage, and 3% perchloric acid in 2–butoxy–ethanol for second-stage.

Atom probe techniques and their applications have been described elsewhere [2,3]. The particular apparatus used here consists of the APFIM200 field ion microscope combined with a reflectron time–of–flight mass spectrometer, an instrument capable of both spatial and chemical resolution on an atomic scale. The chemical analysis can be carried out on atoms which are induced to evaporate from the sample using voltage pulses, the pulse fraction being 20% of the sample tip voltage. The sample temperature was maintained at 60 K throughout the experiments.

RESULTS AND DISCUSSION

A. Chemical Analysis

The mass spectrometer on the APFIM200 gives the time–of–flight of each ionised atom as it is evaporated from the sample tip and eventually detected. These data then have to be converted into mass/charge ratios for the identification of the species concerned [3]. Fig. 2 shows the relationship of isotopic abundances as a function of the mass/charge ratios of the elements that occur in mechanically alloyed steels. It is evident that there is considerable overlap between elements, but the problem is not as severe as might appear at first sight. Much of the overlap is due to isotopes with low abundance, which may be neglected without a great sacrifice to accuracy. This is illustrated in Fig. 3. The reasonable accuracy of this procedure is seen from Fig. 4, where the results from atom probe data seem to compare well against the bulk chemistry of the alloy.

B. Chemical Structure of the Solid Solution

Any solid solution which is in thermodynamic equilibrium (for example, a homogenised phase) will nevertheless exhibit concentration fluctuations of increasing magnitude as the size of the region which is chemically analysed decreases [4,5]. These are random fluctuations which obey the laws of stochastic processes, and represent the real distribution of atoms in the solution. The essential purpose of the present work is to establish whether there exist any concentration fluctuations which are in excess of those expected in a chemically homogeneous solid solution,
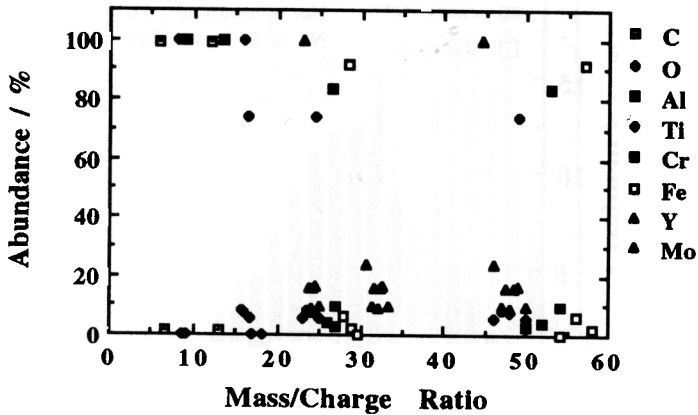
Figure 2. The natural abundance of various ionised species of relevance to the present work.
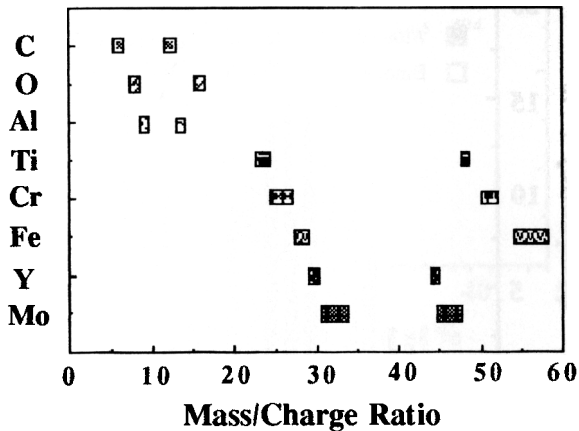

Figure 3. The range file used in the analysis of the atom probe data, after neglecting those species which have a relatively low abundance.
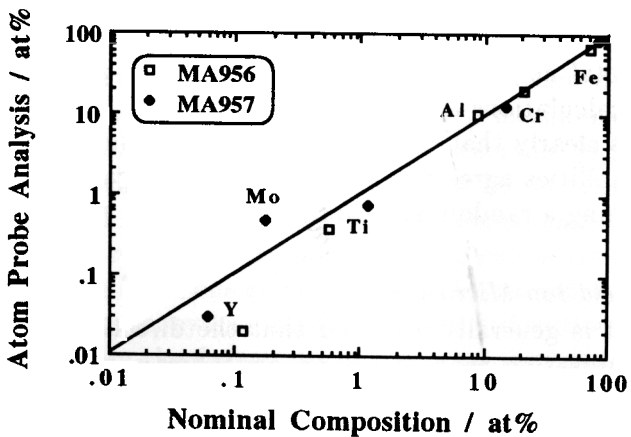

Figure 4. The agreement between the measured and actual bulk compositions of the alloys studied.

and hence to comment on the true atomic state of the solution produced by the mechanical alloying of commercial steels.

The equilibrium fluctuations discussed above cannot usually be observed directly because of the lack of spatial resolution and noise in the usual microanalysis techniques. The fluctuations only become prominent when the resolution of chemical analysis falls to less than about a thousand atoms block. The atom probe technique used here collects the experimental data on an atom by atom basis (*i.e.* the highest conceivable spatial resolution). The analysis also contains no error of the type associated with X–ray emissions where the same area when analysed twice will in general give different results because of the stochastic nature of X–ray emissions. The atom by atom data can be presented at any block size. For convenience of illustration, we use a block size of fifty atoms each.

Fig. 5 illustrates the variation in the chromium concentrations (fifty atom blocks) of the ferrite in *MA956* and *MA957*. Similar data for aluminium are presented in Fig. 6. There are real fluctuations but further analysis is needed to show whether they beyond what is expected in homogeneous solutions

C. Frequency–Distributions

For a random solution, the distribution of concentrations should be binomial since the fluctuations are random; any significant deviations from the binomial distribution would indicate either the clustering of like atoms or the ordering of unlike pairs.

The frequency distribution is obtained by plotting the total number of composition blocks with a given number of atoms of a specified element against the concentration. Fig. 7, Fig. 8, and Fig. 9 show that the experimental distributions are essentially identical to the calculated binomial distributions, indicating that the solutions are random.

D. Pair Probabilities

The atom probe data can be further analysed if it is reasonably assumed that successive atoms picked up by the mass spectrometer were near neighbour atoms in the sample. Successive atoms which are identical then represent bonds between like atoms *etc.* , so that pair probabilities used in solid solution theory can be measured experimentally. These data can be compared against calculated pair probabilities. Thus, in a *random A−B* solution, the probability p_{AB} of finding $A−B$ or $B−A$ bonds (near neighbours) is
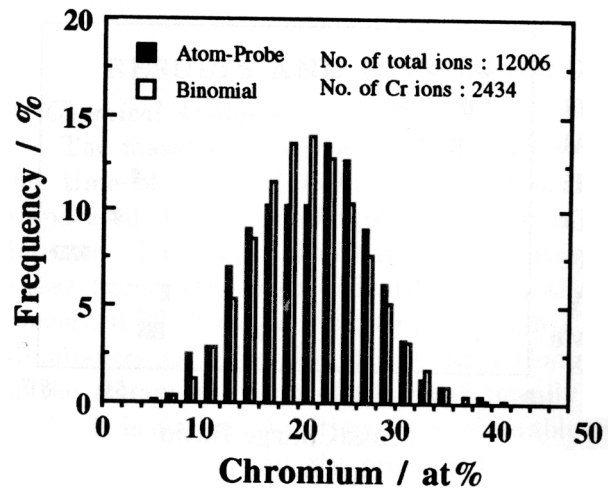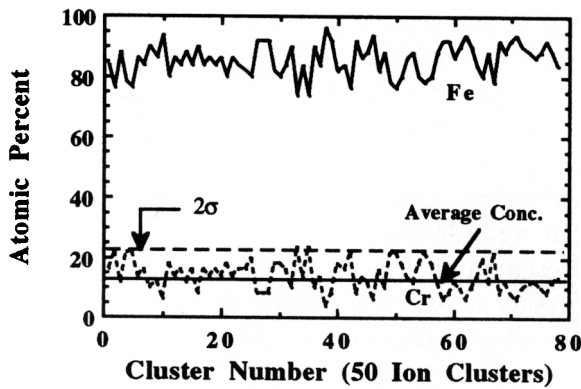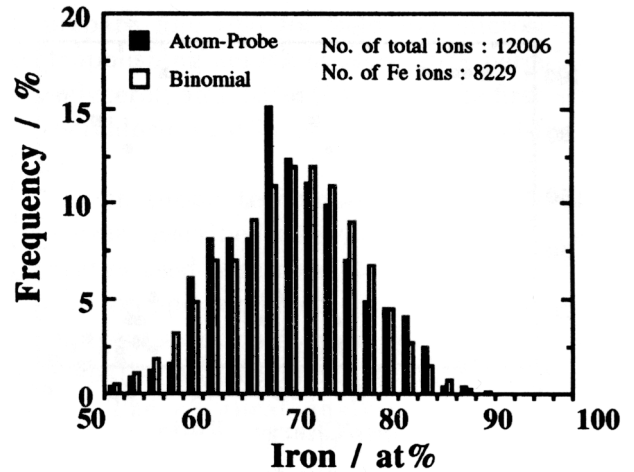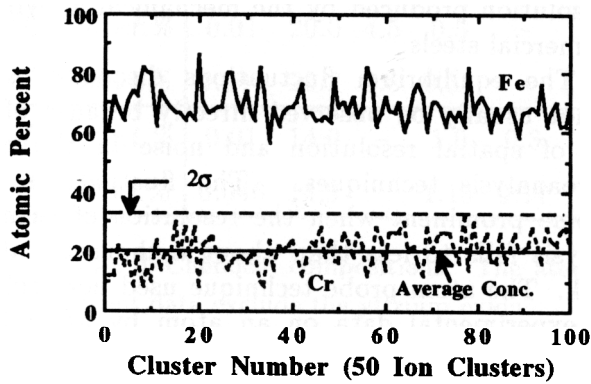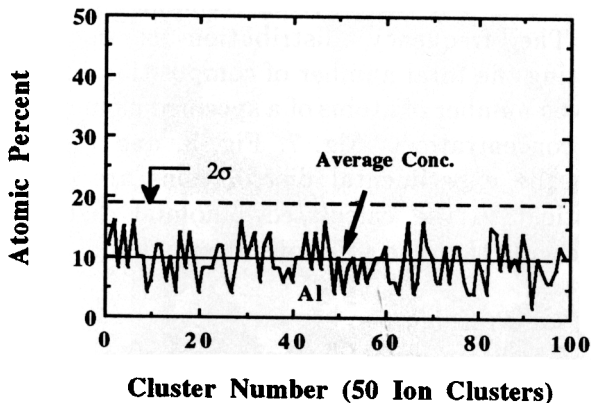
Figure 5. The composition profiles of chromium as a function of depth, in as–received (a) *MA956* and (b) *MA957* steels.

Figure 6. The composition profiles of aluminium as a function of depth, in as–received *MA956* steel.

given by $p_{AB} = 2x_A x_B$ where x_i is the atom fraction of element i. Similarly, $p_{AA} = x_A^2$ and $p_{BB} = x_B^2$. B is the solute element (such as Cr or Al) whereas A represents the remainder of atoms. N represents

Figure 7. Frequency–distribution curves for Fe and Cr in as–received *MA956* steel.

the total number of atoms included in the analysis. The calculations assume a random solution. Table 2 shows clearly that the experimentally measured pair probabilities agree remarkably with those calculated assuming a random solution.

E. Field Ion Microscopy

It is generally accepted that the directional recrystallisation that occurs on annealing a mechanically alloyed nickel–base alloy is a secondary recrystallisation process. The ultrafine-grained equiaxed microstructure produced by primary recrystallisation during fabrication is replaced by a much coarser col-
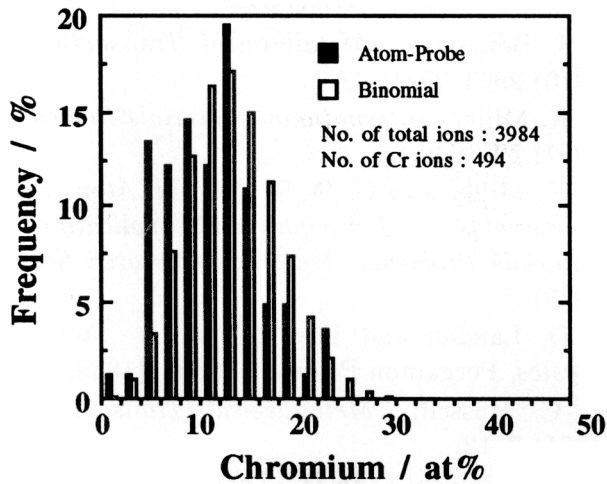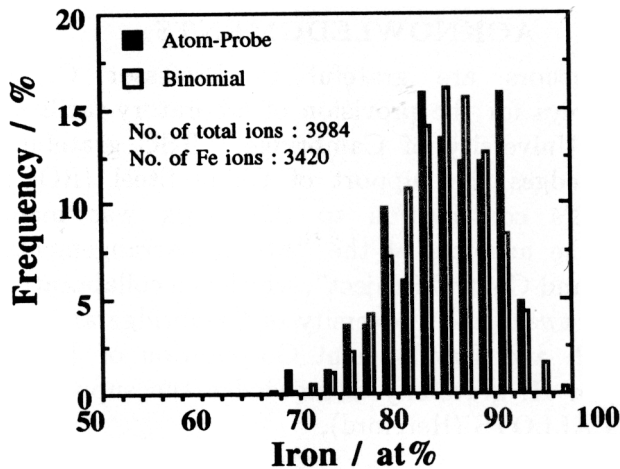
Figure 8. Frequency–distribution curves for Fe and Cr in as–received *MA957* steel.

Figure 9. Frequency–distribution curves for Al in as–received *MA956* steel.

Alloy	Element	p_{AA}	p_{AB}	p_{BB}	N
MA956	Cr (Measured)	0.636	0.323	0.041	12006
MA956	Cr (Calculated)	0.637	0.322	0.041	
MA956	Al (Measured)	0.806	0.184	0.010	12006
MA956	Al (Calculated)	0.832	0.161	0.008	
MA957	Cr (Measured)	0.767	0.217	0.015	3984
MA957	Cr (Calculated)	0.724	0.254	0.022	

Table 2 Pair probability analysis. B is the solute element (such as Cr or Al) whereas A represents the remainder of atoms. N represents the total number of atoms included in the analysis. The calculations assume a random solution.

umnar grain structure [7]. It is often assumed that this scenario also represents iron–base mechanical alloys, but recent evidence suggests otherwise [6,8]. It appears that fabrication leaves these alloys in a cold deformed state, so that subsequent annealing leads to primary recrystallisation to a coarse columnar grain structure [6]. Consistent with this, transmission electron microscopy has revealed a large dislocation density within the flattened fine grains of the fabricated alloy.

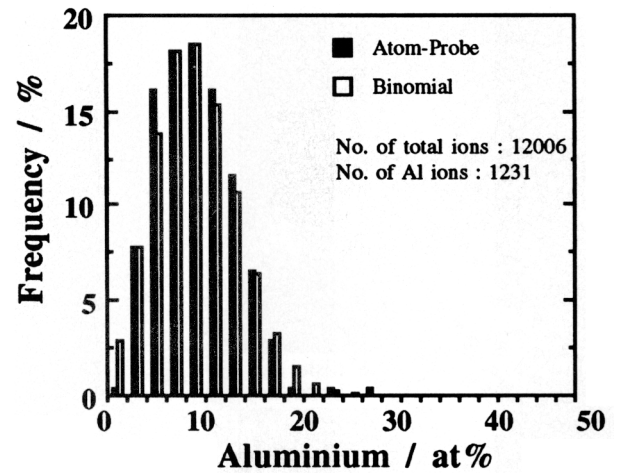The present work confirms that the prior to the formation of the coarse recrystallised grain structure is in fact in the cold deformed state. Field ion microscopy has revealed a fine dislocation cell structure (Fig. 10) on the scale of some 30 nm cell size.

SUMMARY & CONCLUSIONS

It has been demonstrated that the ferrite phases of the iron base mechanical alloys *MA956* and *MA957* consist of a random distribution of atoms. This does not mean that the solutions are thermodynamically ideal, but that the alloy preparation method which involves intense deformation leads to a random dispersal of atoms. This is in spite of the fact that Fe–Cr solutions are known to deviate significantly from
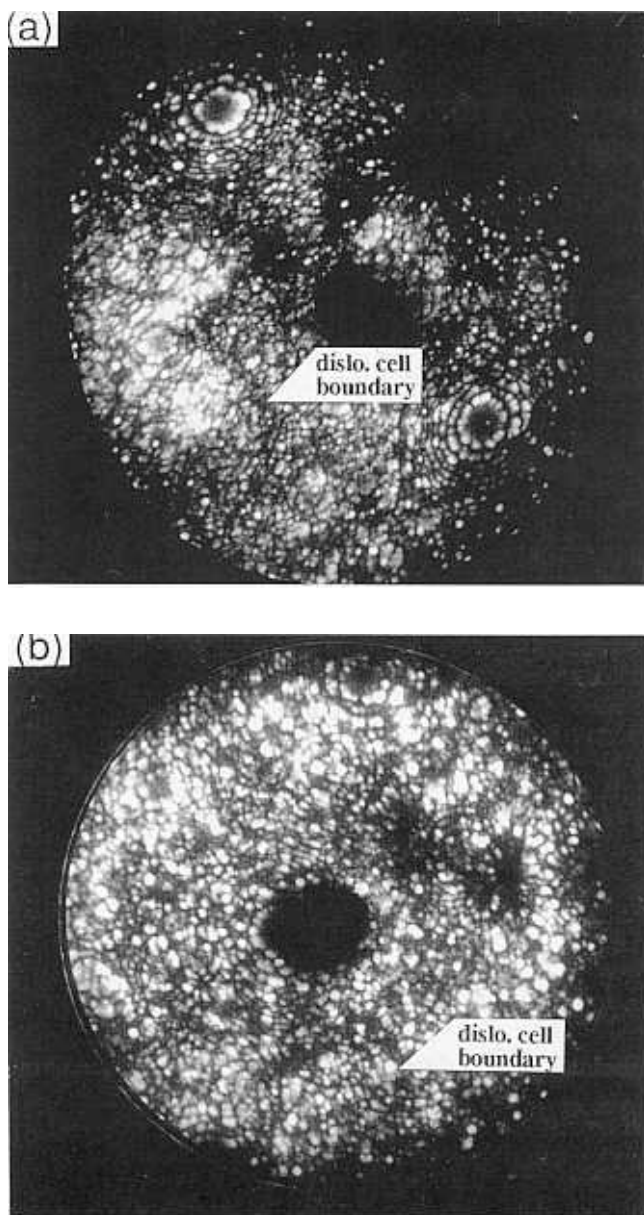
Figure 10. Field ion micrograph of as–received (a) *MA956* and (b) *MA957* steels. The sample temperature is 60 K and the tip voltage about 10 KV.

ideality, with a tendency for like atoms to cluster [9,10]. Thus, it can be concluded that the alloy is in a mechanically homogenised nonequilibrium state, and that prolonged annealing at low temperatures should lead to, for example, the clustering of chromium atoms. This will be the subject of a future study.

Field ion microscopy has also revealed that prior to recrystallisation, the alloys contain fine dislocation cell structures consistent with their cold deformed state.

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