JOURNAL OF MATERIALS SCIENCE 30 (1995) 2738–2742

Reordering, recrystallization and recovery behaviour of $(Co_{0.78}Fe_{0.22})_3$ V as a function of the initial state of order

Part II *Microstructure*

Y. LIN*, S. GIALANELLA‡, R. W. CAHN
Department of Materials Science and Metallurgy, University of Cambridge, Pembroke Street, Cambridge, UK

Optical and electron micrography were used to examine the progress of recovery and recrystallization in the (Co–Fe–V) alloy rolled in the initially disordered state and annealed at a range of temperatures, and the results were related to the measurements reported in Part I of this study. The indirect results include a plot of fraction recrystallized at various temperatures against annealing time: unexplained anomalous behaviour was found at the highest temperature. Stacking-faults and antiphase domain boundaries in the recrystallized grains were examined.

1. Introduction

The first part of this study [1], hereafter referred to as I, was mainly concerned with the reordering and recovery kinetics after different thermo-mechanical treatments of the $L1_2$ intermetallic compound $(Co_{0.78}Fe_{0.22})_3V$. In line with the results of a previous study of this same material [2] and also of I, we found in this second part that, for the same annealing conditions, the kinetics in the deformed alloy are influenced by the state of long-range order (LRO) of the alloy before it was deformed. This happens because, if the material was originally disordered, on annealing recovery and recrystallization compete with the reordering process; if it was originally fully ordered (and then only very partially disordered by the deformation), that competition is less pronounced. The complexity of the consequential changes was shown by the resistometric and calorimetric measurements presented in I.

The presence or absence of LRO affects the recovery and recrystallization kinetics in distinct ways. Diffusion-driven phenomena, such as vacancy recombination and grain-boundary migration, and indeed reordering itself, are always hindered by the presence of LRO and this can delay recrystallization. Dislocations, active during the recovery stages, can readily move in the ordered matrix only when pairs of partials join together to form superdislocations. In the hope of gaining a better understanding of the results reported in I, which were based entirely on resistometric, calorimetric, X-ray diffraction and hardness measurements, we undertook a limited microstructural investigation, focused on the evolution of microstructure induced by anneals, at several temperatures, of samples disordered before rolling: these showed the most striking variations of hardness during annealing. The emphasis here is on the degree of recrystallization attained at various stages of annealing, and to a lesser extent on the striking strain–age-hardening reported in I.

2. Experimental procedure

Some of the samples which had been used for hardness tests were selectively etched in Marble's reagent for optical observations. This etchant, combined with the use of a Nomarski objective, gave adequate contrast to identify recrystallized regions. The recrystallized fraction was then approximately estimated by manual image analysis of a substantial field of view. (The recrystallized grains could be more clearly distinguished under the microscope than from photographs.)

Thin sections were prepared for transmission electron microscopy (TEM) in the usual way. Jet-polishing was done with a 12.5 vol % solution of H_2SO_4 in methanol at $-10\,^{\circ}C$. Observations were performed with a Philips 400 ST instrument.

3. Results

Optical observations were made on samples of the LRODR (initially disordered, then rolled 50%) samples annealed at four temperatures: 500, 720, 770 and

* *Permanent address*: Shanghai Iron and Steel Research Institute, 1001 Tai He Raod, Wuson, Shanghai, China
‡ *Permanent address*: Dipartamento di Ingegneria dei Materiali, Universitá di Trento, 38050 Mesiano di Povo, Trento, Italy

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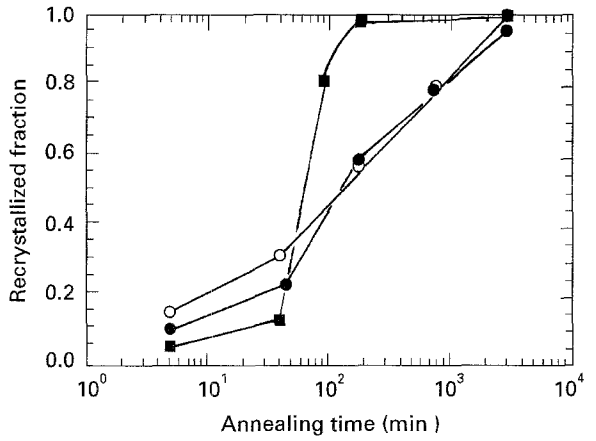


Figure 1 Initially disordered alloy, rolled to 50% reduction: recrystallized fraction, deduced by analysis of optical microscope images, as a function of annealing time at three temperatures. ■ 850 °C; ○ 770 °C; ● 720 °C.

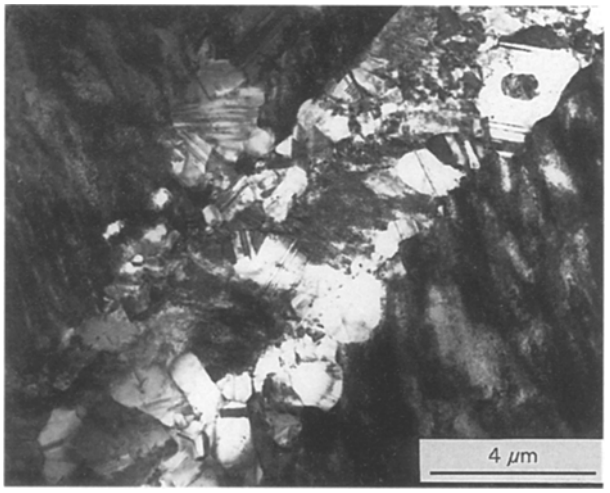


Figure 2 Initially disordered alloy, rolled to 50% reduction: transmission electron micrograph of recrystallized grains at a prior grain boundary, after 10 min anneal at 850 °C.

850 °C, for times ranging from 5 min to 96 h. At the lowest temperature, no sign of recrystallization was seen, even after 96 h. The samples contained fine precipitates which were identified as vanadium carbides, as reported in an earlier study [3] and further discussed below.

The optical examination showed that early stages of recrystallization, with the appearance of new grains, are detectable already after a 5-min anneal at 720 °C, 770 °C or 850 °C. These new grains were formed and grew mainly in the neighbourhood of the old grain and twin boundaries. Comparing the recrystallized fractions, it can be seen, surprisingly, that recrystallization proceeds more rapidly at the two lower temperatures than at the highest temperature. This remains true up to about 40 min (Fig. 1), but then the trend changes and recrystallization accelerates greatly at 850 °C, being almost complete after 2 h, at which time it is still far from complete at the lower temperatures.

A series of samples only thermally disordered and not rolled (LROD, in the terminology of I) did not

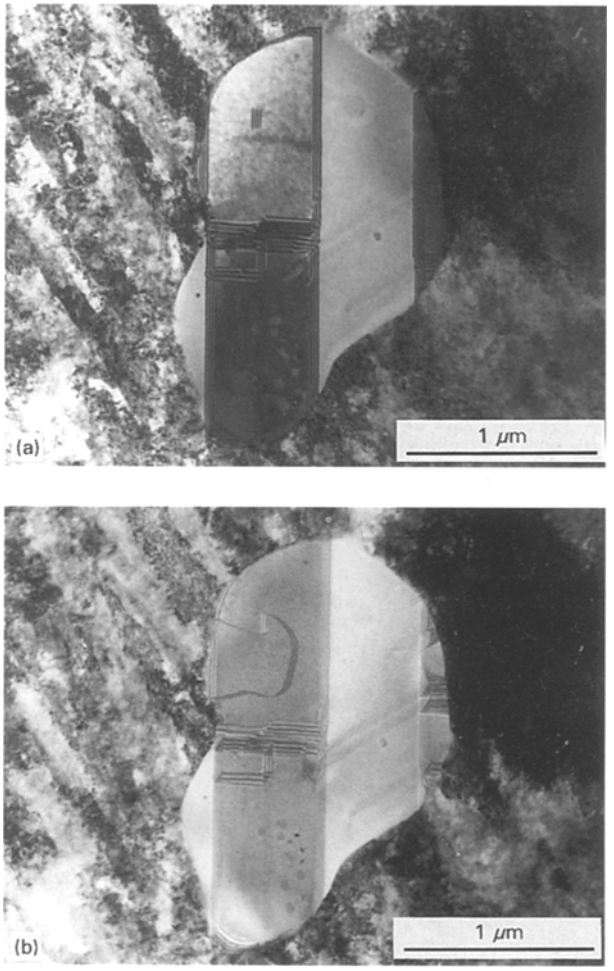


Figure 3 As Fig. 2, isolated recrystallized grain in prior grain interior. (a) Bright field: (b) dark field.

show any signs of change in the grain morphology on annealing at 770 °C and 850 °C. Annealing only changes the degree of LRO and there is no driving force for recrystallization.

Several LRODR samples were selected for TEM observations. The as-deformed samples were too full of dislocations to permit satisfactory micrography. The dislocation density remained very high after annealing for a few minutes, but for the highest temperature only (850 °C) some areas of lower dislocation density were seen in the dislocation forest: this was the only evidence of "recovery" observed. At this stage, newly nucleated grains (often containing annealing twins) were seen at grain boundaries of the deformed structure (e.g. Fig. 2), and occasional new grains were also seen in the grain interiors. Selected-area diffraction patterns at this stage showed clear superlattice spots; there was no difference in this respect between the deformed matrix and new grains.

Fig. 3 shows a pair of micrographs of a small grain in the grain interior after 10 min at 850 °C, (a) with bright field (BF), (b) with dark field (taken with the superlattice vector $\mathbf{g} = 100$). This grain is one of the rare cases where antiphase domain boundaries (APDBs) were seen in a new grain; the APDB is connected to a stacking-fault, visible in both micrographs. Traces of small particles of a second phase are also visible in this grain. By means of microdiffraction,

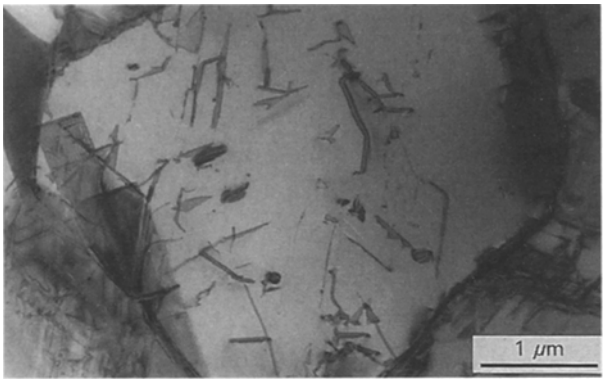


Figure 4 Initially disordered alloy, rolled at 50% reduction: dislocations in a recrystallized grain, after 24 h anneal at 850 °C.

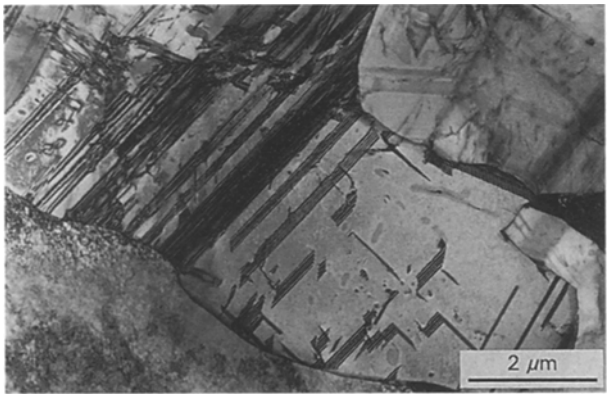
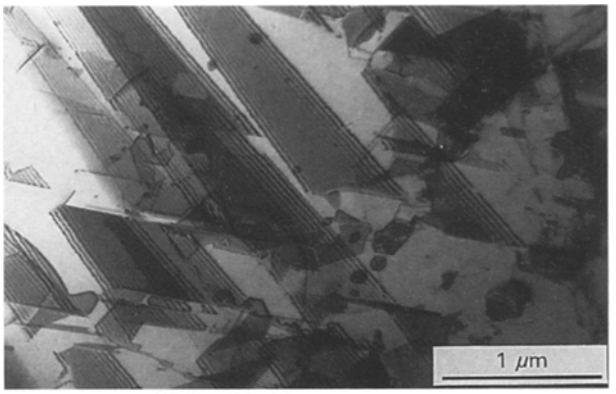


Figure 5 Initially disordered alloy, rolled to 50% reduction: bright-field image of a recrystallized grain with stacking-faults, after 48 h anneal at 720 °C.

these were identified as f.c.c., with a lattice parameter of ≈ 0.41 nm. These findings identify the particles as VC precipitates: we could note no particular orientation relation between the new grain and the various precipitates, which indicates that they were formed before the recrystallization had started, during alloy preparation or during the disordering heat-treatment. Dislocations were sometimes seen in new grains, like the one in Fig. 4 (sample annealed 24 h at 850 °C): the dislocations here are all paired ones, i.e. superdislocations.

Fig. 5 shows a BF image of a recrystallized grain (still surrounded by deformed matrix) in a sample annealed 48 h at 720 °C. Stacking-faults were quite common (though not universal) in recrystallized grains, and many of these can be seen in the micrograph. Some stretch right across the grain, some are bounded at one end or at both by partial dislocations. Some of these defects, as in Fig. 3, are connected to APDBs. The two DF micrographs of Fig. 6 show stacking-faults in a new grain formed at 850 °C: for the two images, **g** vectors with the same direction but opposite sense were used, (1 1 1) and $(\bar{1}\,\bar{1}\,\bar{1})$. The asymmetric sequence of fringes in the DF images here indicate the intrinsic character of these defects. On the basis of extensive sampling and orientation analysis, we concluded that the majority of the stacking-faults seen are of this kind, i.e. intrinsic and preferentially lying on {1 1 1} planes.



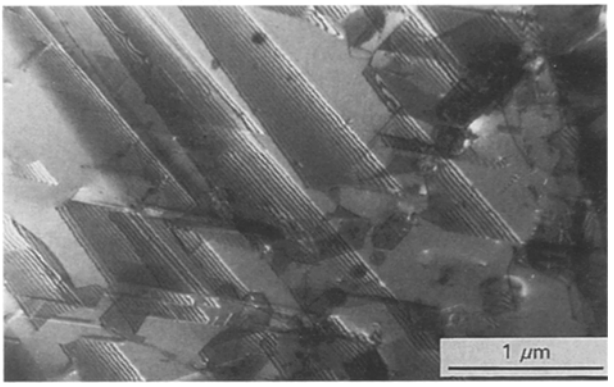


Figure 6 Initially disordered alloy, rolled to 50% reduction: two dark-field images of a recrystallized grain with stacking-faults, after 24 h anneal at 850 °C.

4. Discussion

The optical observations of the LRODR samples shed some light on the hardness variation upon annealing reported in I: the most important features are shown again here, in Fig. 7. It was argued in I, on the strength of measurements of the Bragg order parameter, S, as a function of annealing, that the peak in hardness in this plot is to be attributed to an increase of LRO, with a maximum hardness arising for $S \approx 0.5$. What it was not possible to judge in I was how far the drop in hardness beyond the peak was attributable to the increasing perfection of LRO, and how far it was associated with progressive recrystallization. Comparing Fig. 7 with Fig. 1, it is clear that recrystallization causes the larger part of the softening, but that subsequent events, perhaps grain growth, are also implicated. The hardness curve for 850 °C has returned to its as-deformed hardness after 10^2 min, at which point (see Fig. 2) recrystallization is almost complete. If recrystallization were the only factor involved, the hardness should at this point be far below the as-deformed level. According to our X-ray diffraction (XRD) measurements (I, Fig. 11) the order parameter after 100 min at 850 °C has reached ≈ 0.8, which is far enough removed from perfect order to account for a measure of residual order-hardening. The further softening after 100 min would then be due partly to further ordering and partly to grain growth; it is not possible to quantify the shares of the two factors from this curve alone. Stacking-faults in recrystallized grains (see below) are a further complication.

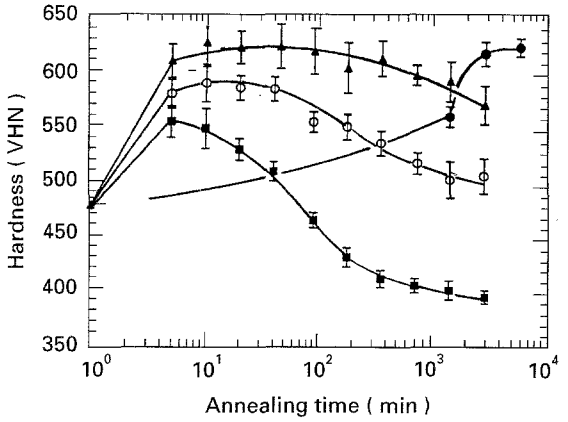


Figure 7 Hardness of initially disordered alloy, rolled to 50% reduction, annealed at (●) 500 °C; (▲) 720 °C; (○) 770 °C; (■) 850 °C.

The fact that the 770 °C isotherm in Fig. 7 lies so far above the 850 °C isotherm, in spite of the fact that the long-range ordering kinetics at the two temperatures are virtually identical (I, Fig. 11) – these temperatures being presumably respectively below and above the time–temperature–transformation "nose" – indicates clearly that the recrystallization share in determining the hardness must be a substantial one. After 1000 min at 770 °C, the hardness has not yet returned to its starting value, though ordering is certainly complete. At this point in time, the recrystallized fraction at the two temperatures is substantially different. The conclusion seems to be that the large difference in hardness at this point, some 120 units, is largely due to the difference in the progress of recrystallization (and subsequent grain growth). Further than this one cannot go.

The observations have given no direct clue as to the origin of the anomaly in the form of the recrystallization curve for 850 °C with its break after 40 min. However, we have found some evidence that dislocation recovery operates at this high temperature in the unrecrystallized part of the microstructure and this must serve to soften the alloy overall even before recrystallization begins; indeed, this may be the reason for the delayed inception of recrystallization.

Our observation of a preponderance of nucleation of new grains near grain boundaries is consistent with earlier studies, notably one on Co_3Ti [4]. There has been a whole series of studies of the linkage of ordering and recrystallization in alloys such as FeCo [5, 6] and Ni_2V [7]: these are alloys in which, in a certain temperature range, ordering takes place heterogeneously, i.e. behind an advancing grain boundary, so that in this range ordering and grain growth are indissolubly linked. This kind of complication does not arise with $L1_2$-type compounds such as the one we have studied here. These matters have been reviewed by one of the authors [8].

Our observations of stable stacking-faults in recrystallized grains (and of very occasional APDBs) are in accord with the earlier study by Braski *et al.* [3]. They found both intrinsic and extrinsic stacking-faults at different annealing times. They also found that these faults were nucleated at the pre-existing VC precipitates, as a result of the dissociation of superdislocations which themselves were generated by the release of the elastic strain built up at the carbide–matrix interface. Some of these conclusions were later questioned by Pope and Ezz [9]. It is not our aim here to resolve these disagreements, but only to point out the notable stability of these defects and the likelihood that their presence enhances the hardness of the recrystallized grains. This may be one reason why the hardness of fully recrystallized specimens may still be above that of the initial deformed material.

5. Conclusions

1. The strain-age-hardening of the LRODR samples is due to the gradual increase of LRO, and peaks when the order parameter ≈ 0.5.
2. Recrystallization only proceeds at a detecta ble rate above about 700 °C in LRODR material (i.e. n aterial which had been thermally disordered before r lling).
3. New grains form predominantly at grain l oundaries but a few form in grain interiors.
4. At the highest temperature used, 850 °C, there is some dislocation recovery in the cold-w(rked LRODR matrix, which must act to lower the ove:.ll hardness of the material.
5. In the recrystallized grains, few APDBs were observed, but there were copious stacking-faults which were stable against further annealing.
6. The changes in hardness during the annealing of the deformed alloy are caused jointly by changes in the order parameter and by progressive recrystallization and grain growth, with some contribution from matrix recovery at the highest temperature and presumably from the presence of stacking faults in the recrystallized grains.
7. The combination of XRD and microscopy indicate that the initial fast exponential processes recorded by the isothermal resistometric measurements are mainly associated with reordering.

Acknowledgements

We are deeply indebted to Dr C. T. Liu, of Oak Ridge National Laboratory, USA, for providing the alloy sheets used in this research.

The work was supported by the Commission of the European Communities, DG XII, under contract SCI-0262-C, more recently replaced by contract CHRXCT930324. We are grateful for this support.

Y. L. is indebted for personal support during his stay in Cambridge to the State Education Commission of the Chinese Government.

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Received 22 August
and accepted 10 October 1994