JOURNAL OF MATERIALS SCIENCE 28 (1993) 538–546

Reordering, recrystallization and recovery behaviour of $(Co_{0.78}Fe_{0.22})_3V$ as a function of the initial state of order

Part I *Kinetics*

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The ordering kinetics of the $L1_2$ alloy $(Co_{0.78}Fe_{0.22})_3V$ have been studied on annealing below the order–disorder transition temperature and starting from different initial conditions induced by different thermo-mechanical treatments. The results obtained are reported in two parts. In Part I, we have determined by means of dilatometric, resistometric and calorimetric analysis, the relevant temperatures and energies dissipated in the transformations, and how the rates are affected by the initial conditions and annealing temperatures. The variation of hardness and the long-range order parameter have also been measured. The results obtained suggest that the overall kinetics are dependent on the way in which ordering, recrystallization and recovery phenomena occur at different temperatures and on how they affect each other.

1. Introduction

Recovery, recrystallization and reordering in several orderable intermetallic compounds have recently been reviewed [1]. These phenomena in such materials present a large variety of aspects, strongly dependent on the order conditions in which the deformations are introduced, and on the relative rates at which recovery, recrystallization and reordering occur. This is because dislocation arrangement and dynamics are very sensitive to the degree of order, and diffusion-driven processes such as grain-boundary migration are usually hindered and slowed down by an ordered atomic configuration.

The first systematic work on the interplay between ordering, recrystallization and recovery was carried out by Roessler *et al.* [2] on Cu_3Au. Several specimens were cold-rolled to 63% reduction in their ordered and disordered states. In both cases, an increase in hardness was observed upon annealing at 288 °C, i.e. order-hardening. This effect was larger in the strained samples than in those thermally disordered but not strained. The strain-hardening too was sensitive to the initial condition, being larger in the samples rolled in the ordered state. All the hardness versus annealing time curves showed maxima, occurring before complete re-establishment of the long-range order; also the initially ordered samples were partially disordered by the mechanical deformations. Order-hardening has been observed in other intermetallics also, some thermally disordered, others cold-worked.

The ordering kinetics of Cu_3Au and other $L1_2$ compounds, Ni_3Fe and Ni_3Mn, was investigated by Davies and Stoloff [3]. The hardening observed during isothermal annealings of disordered specimens was attributed to the joint action of short-range order and the creation of antiphase domain boundaries (APDBs). Regions of incipient order, full of APDBs, can, in fact, hinder the motion of single dislocations such as are present in the disordered state. Similar effects were observed in orderable alloys with other structures, such as the hexagonal close-packed ordered alloy Mg_3Cd [4]. Ordering in the Cu–Pt system, with a rhombohedral ordered structure, was studied as a function of composition and temperature. In this case the ordering-hardening was attributed to the formation of ordered domains and to the misfit arising from their different orientations [5]. The interaction between single dislocations and the partially ordered structure is the main reason for the peak in the yield strength observed in the cubic ordered alloys

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Fe_3Al and FeCo, DO_3 and B2, respectively [6]. As reordering goes on, the single dislocations eventually join together to form pairs and, as superdislocations, can move more easily in the ordered material. Unlike in Cu_3Au, in these alloys the strain-hardening was not affected by the order conditions in which they were deformed.

A common finding of these and other studies is that the hardness (or yield strength) maxima observed during reordering always arise for an intermediate degree of order. This has once more been dramatically proved in a recent investigation on disordering and amorphization of Ni_3Al powders by means of mechanical attrition in a vibratory mill [7]. The heavily deformed Ni_3Al, as it is progressively disordered by deformation, reaches a very high hardness peak when the long-range order parameter, S, is equal to 0.5, and then softens again as S sinks toward zero. This finding has been recently confirmed by a study on cold-rolled Ni_3Al [8]. The level of cold-rolling used induced only a limited disordering, to $S = 0.7$. No increase in yield stress and only a minor order-induced increase of indentation hardness were observed in this case on annealing the samples at several temperatures.

In the present study, part of a wider European research project on "Ordering Kinetics in Alloys", we have examined the reordering, recrystallization and recovery behaviour in the $L1_2$ orderable compound $(Co_{0.78}Fe_{0.22})_3V$. This alloy, under the code name LRO-1, belongs to a family of compounds widely and thoroughly characterized at Oak Ridge National Laboratory by a group led by Liu [9], who kindly made available the sheet of material used for this research. The objective was to complement a previous investigation, in which this same material was cold-rolled in the initially fully ordered state and then annealed [10]. This alloy is particularly suitable for such an investigation for several reasons: a comparatively high order–disorder transition temperature (910 °C), the possibility of retaining the disordered phase at room temperature by water-quenching from above T_c, and a relatively high ductility at room temperature. We have divided the presentation of our results into two parts. Part I is mainly concerned with the reordering kinetics of disordered and cold-rolled specimens followed by hardness tests, resistometric measurements, differential scanning calorimetry, dilatometry and X-ray diffraction. The second, complementary, part (Part II, [11]) is mainly based on micrographic observations. Several specimens were analysed at different stages of isothermal anneals by means of optical and electron microscopy. This was done in an attempt to clarify the questions raised in Part I.

2. Experimental procedure

A piece of sheet, which had been cold-rolled to 25% reduction in the originally fully ordered state, was disordered by water quenching after heating to 1100 °C for 90 s. As reported earlier [10], this treatment is sufficient also to obtain complete recrysallization of material. To prevent oxidation, the sample was kept in flowing argon during the heat treatment. Then it was cold-rolled to a final reduction of 50%. Several pieces were cut off and sealed in silica tubes, isothermally annealed at 500, 720, 770 and 850 °C for times ranging from 5 min to approximately 48 h. Longer annealing times were used at $T = 500$ °C (from 24–96 h). To define the annealing times, each anneal was stopped by dropping the sample into water.

Hardness tests were carried out with a Leitz Miniload 2 instrument using a 500 g load. Ten indentations, well distributed on the surface of each sample, mounted in resin and metallographically polished, were performed to evaluate the average value and its standard deviation.

Resistometric measurements were performed, both in continuous heating and isothermal modes on several samples, to study their reordering kinetics and the annealing out of the defects introduced with the thermomechanical treatments. The resistance of strip-like specimens, placed in a vertical furnace in a helium atmosphere, was measured by the usual four-contact method. Several thermocouples were used for monitoring the temperature of the specimen and for the input of the heating controller. An IBM-PC, with software developed for the purpose, was used for automatic data acquisition and analysis.

Calorimetric tests were carried out to measure the enthalpy output accompanying the phenomena occurring upon heating the samples. A Perkin–Elmer DSC 7 instrument was used, mainly operated in the continuous heating mode with scan rates ranging from 5–80 K min^{-1}. The sample, kept under a pure argon atmosphere, after cooling to room temperature, was again run under identical conditions to establish the base line. The apparent activation energies of the relevant processes were estimated with the Kissinger peak-shift method.

A few dilatometric results are also reported, mainly continuous heating and cooling cycles giving further information about the relevant temperatures of the transformations occurring during the reordering and recovery processes.

The evolution of the long-range order parameter, S, of the specimens initially disordered and then cold-rolled was followed by means of X-ray diffraction (XRD), with a Philips wide-angle diffractometer using CrK_α monochromated radiation: because of the anomalous scattering from vanadium atoms, the superlattice line intensities were enhanced with this radiation above the intrinsically low level which results from the similarity of the atomic numbers of cobalt, iron and vanadium. The values of S were calibrated by reference to an unworked sample which had been annealed for 3 days at 850 °C and then slowly cooled. This sample was taken to have $S = 1$. In this way the problem of preferred orientation could be sidestepped.

3. Results

3.1. Thermoanalytical data

The thermoanalytical results are grouped together on the basis of the three different series of samples analysed: (1) LRO-1 thermally disordered (LROD);

(2) disordered and cold-rolled by 50% (LRODR); (3) cold-rolled by 25% in its initially fully ordered condition (LROOR).

A series of continuous heating and cooling resistometric cycles was carried out up to a maximum temperature of about 1060 °C, with some LROD samples. Fig. 1 shows the curves obtained at two different heating rates: 2 and 8 °C min^{-1}. The equilibrium order–disorder transition is clearly detectable from the sharp fall in the resistance to a temperature of about 910 °C, which is in agreement with the value determined by dilatometry [10]. The slight shift in the transition temperature, recorded at different heating rates, is probably due to the fact that different samples were used for each test, having minor differences in composition and defect configuration. As expected for a first-order transition, there is a sharp change in the resistance [12]: in fact, the atomic arrangement remains almost unchanged up to the transition temperature, and the long-range order parameter drops only slightly from the room-temperature value, down to about 0.8, over a large temperature range. The bump just below T_c (see Fig. 1) is a typical feature already observed in other orderable compounds [13, 14]. As pointed out in a previous study on the ordering kinetics of the DO_3 ordered compound Fe_3Al [15], mainly two factors affect the dependence of the resistivity in these ordered alloys on temperature: the mobility of the conduction electrons, usually decreasing with increasing order; and the frequency of electron scattering from the atoms – this is lower, the higher is the degree of order. The observed results will depend on the relative variations of these two factors when the long-range order is changing. An alternative model takes into account the variations in the structure of the conduction electron band in the neighbourhood of the Fermi surface, induced by changes and relaxations of the long-range order parameter [16]. The resulting effective number of conduction electrons is the parameter which controls the resistivity dependence on the degree of long-range order.

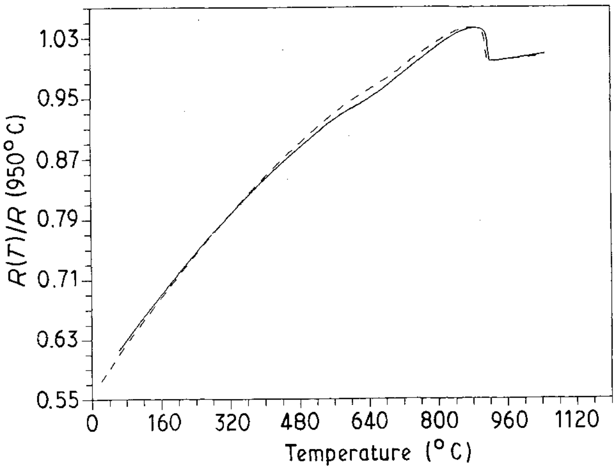

Figure 1 Resistometric continuous heating runs, at (——) 2 and (– – –) 8 °C min^{-1}, for the sample $(Co_{0.78}Fe_{0.22})_3V$ thermally disordered.

The lack of any significant shift in the transition temperature position, on changing the heating rate, indicates a low activation energy for the transformation. However, the transformation occurring over the temperature range 450–700 °C is detectably shifted by changing the heating rate, as shown in Fig. 1. This is presumably due to the recombination of defects, specifically vacancies, which were frozen into the material during the disordering procedure. This transformation takes the material from the metastable disordered state, at $T < T_c$, back to the ordered one. It is interesting to compare the resistometric curves with the dilatometric ones from [10], shown in Fig. 2, for an equivalent sample: both transitions are evident in the dilatometric curve too. Also important is the contraction observed after the first heating and cooling cycle, which corresponds to the level of order restored during the treatment. In this case it is about 0.4%. The total enthalpy release is 46 J g^{-1}, as measured by differential scanning calorimetry (DSC). The temperature range accessible to this instrument allows measurements to be done in the reordering interval. Fig. 3 is the thermogram obtained at the scan rate of 5 °C min^{-1} for a specimen of the series LROD. The reported enthalpy was evaluated by subtracting from the area under the curve that under the baseline, obtained for the same sample from the second heating

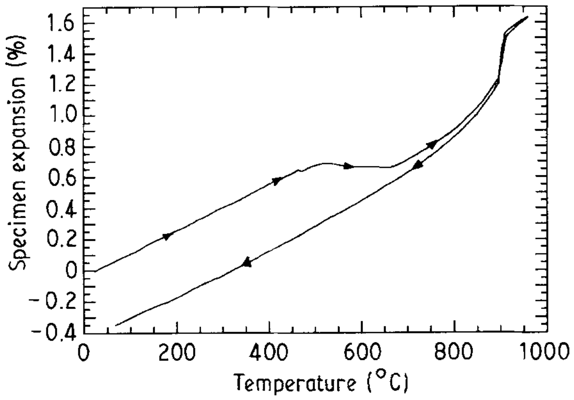

Figure 2 Dilatometric runs, heating and cooling rate 3 °C min^{-1}, for the same sample as Fig. 1: $(Co_{0.78}Fe_{0.22})_3V$ thermally disordered (adapted from [10]).

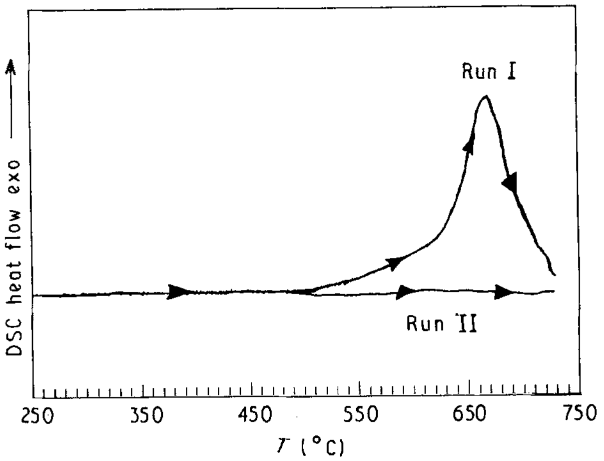

Figure 3 Calorimetric curves of thermally disordered $(Co_{0.78}Fe_{0.22})_3V$. Second run used as baseline. 10 k min^{-1}.

and cooling cycle. From the shape of the calorimetric peak we understand that the overall transformation is actually a complex process. Unfortunately, it spreads just beyond the upper temperature limit of the calorimeter, and this introduces some indeterminacy in the calculation of the total energy output, because of the difficulty of determining a reliable baseline. Nevertheless, this and the following enthalpy values give an approximately correct value of the energy involved in the transformations.

The resistivity curves of Fig. 4 illustrate the annealing behaviour of an LROOR specimen. Again we noticed the sharp fall in the resistance to the equilibrium transition temperature, whose position is, as in the previous case, virtually insensitive to any variation in the heating and cooling rates. In this sample the concentration of defects introduced during rolling is rather small, at least judging from the very weak deflection of the heating branch of the curve, in the range 450–700 °C. The corresponding dilatometric test, Fig. 5, accordingly shows a smaller residual contraction after the first heating and cooling cycle: for this sample is about 0.13%. Finally, the calorimetric results give further support to this picture, by confirming that the structural disorder introduced by rolling an ordered specimen by 25% is rather small: no reliable evaluation of the small enthalpy output could, in fact, be achieved.

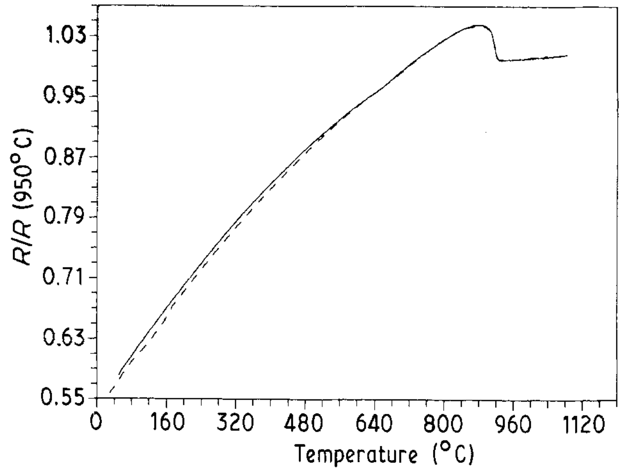

Figure 4 Resistometric continuous heating runs of the samples $(Co_{0.78}Fe_{0.22})_3V$ 25% cold-rolled in the ordered state. (——) 2 °C min^{-1}, (– – –) 8 °C min^{-1}.

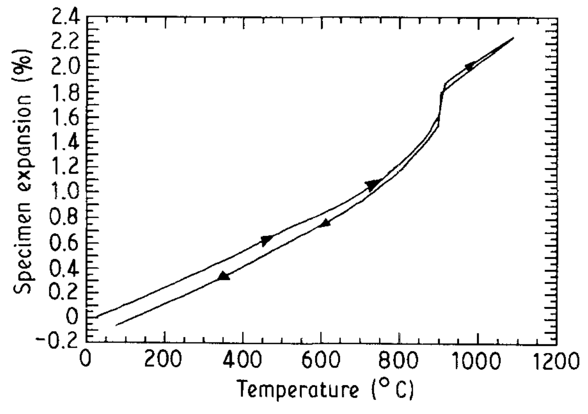

Figure 5 Dilatometric runs of the sample 25% cold-rolled in the ordered state (adapted from [10]).

The combination of thermal disordering followed by mechanical deformation resulted in a heavily disordered structure: sample LRODR. Again the resistometric tests gave a clear evidence of an enhanced concentration of defects, which anneal out during the ordering process and generate a consistent variation in resistivity, Fig. 6; it is much larger than that observed in the previous curves. The calorimetric cycle (Fig. 7, Curve I) shows a broad peak, which almost completely disappears after the first run (Fig. 7, Curve II, used as baseline). The estimated enthalpy of the transformation is 54 J g^{-1}, slightly higher than in the samples just thermally disordered.

Several isothermal resistometric measurements were carried out to investigate the kinetic aspects of the various reordering processes. Three temperatures were selected for this purpose: 650, 700 and 770 °C. In each case an acceptable temperature stability was achieved after few minutes. Fig. 8 shows the typical curves of the resistance relaxation with time at 650,

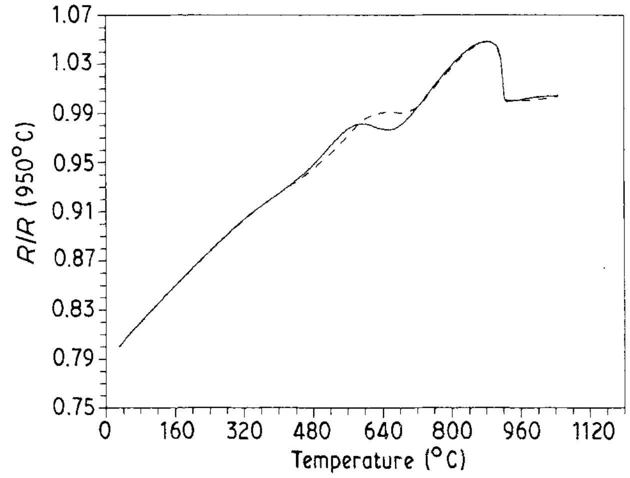

Figure 6 Resistometric continuous heating runs of the samples $(Co_{0.78}Fe_{0.22})_3V$ 50% cold-rolled in the disordered state. (——) 2 °C min^{-1}, (– – –) 8 °C min^{-1}.

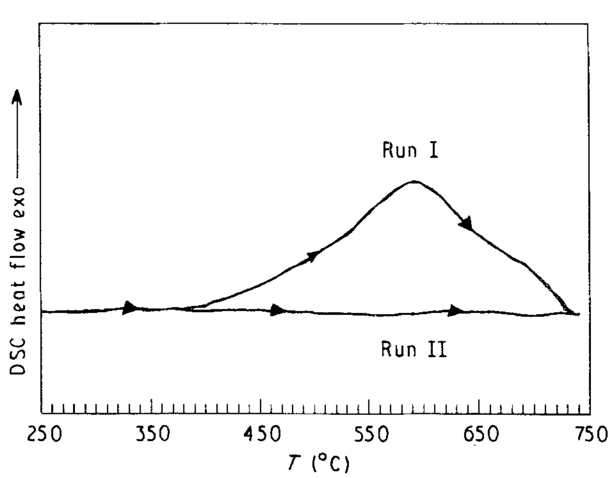

Figure 7 Calorimetric runs of the samples $(Co_{0.78}Fe_{0.22})_3V$ 50% cold-rolled in the disordered state. Second run used as baseline. 10 k min^{-1}.

700 and 770 °C for the sample LRODR. The curves could be fitted with different combinations of exponential and linear functions. Specifically, the ones taken at the two lower temperatures were liable to be fitted with exponentials for the first stages of the process, followed by a linear tail for longer times. This last trend was absent at 770 °C, the highest temperature for isothermal resistometric temperatures: two exponentials were used in this case for fitting the experimental curves.

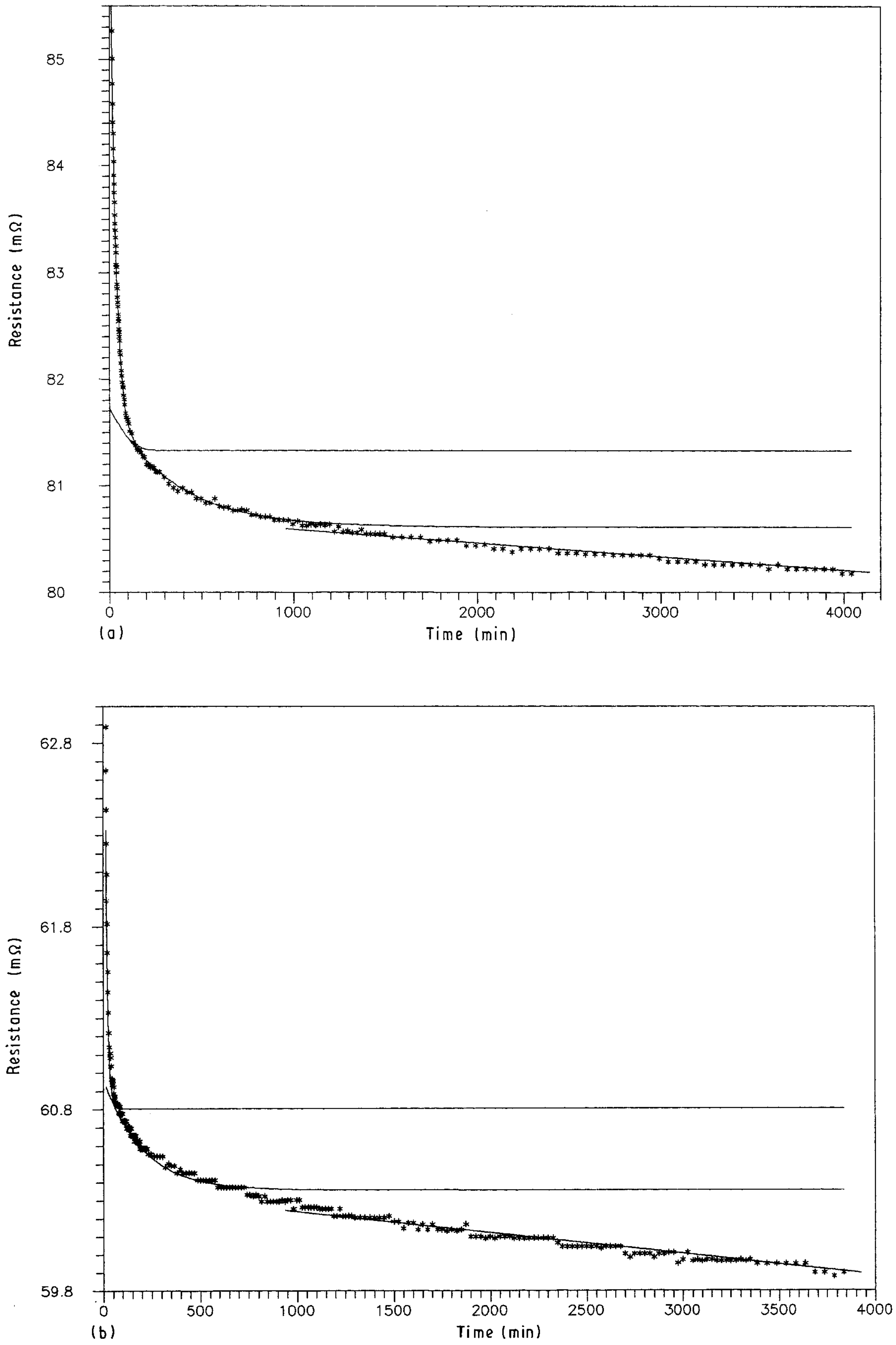

Figure 8 Isothermal resistometries of the samples $(Co_{0.78}Fe_{0.22})_3V$ 50% cold-rolled in the disordered state: 650 °C, (a) *T*, (b) 700 °C (c) 770 °C.

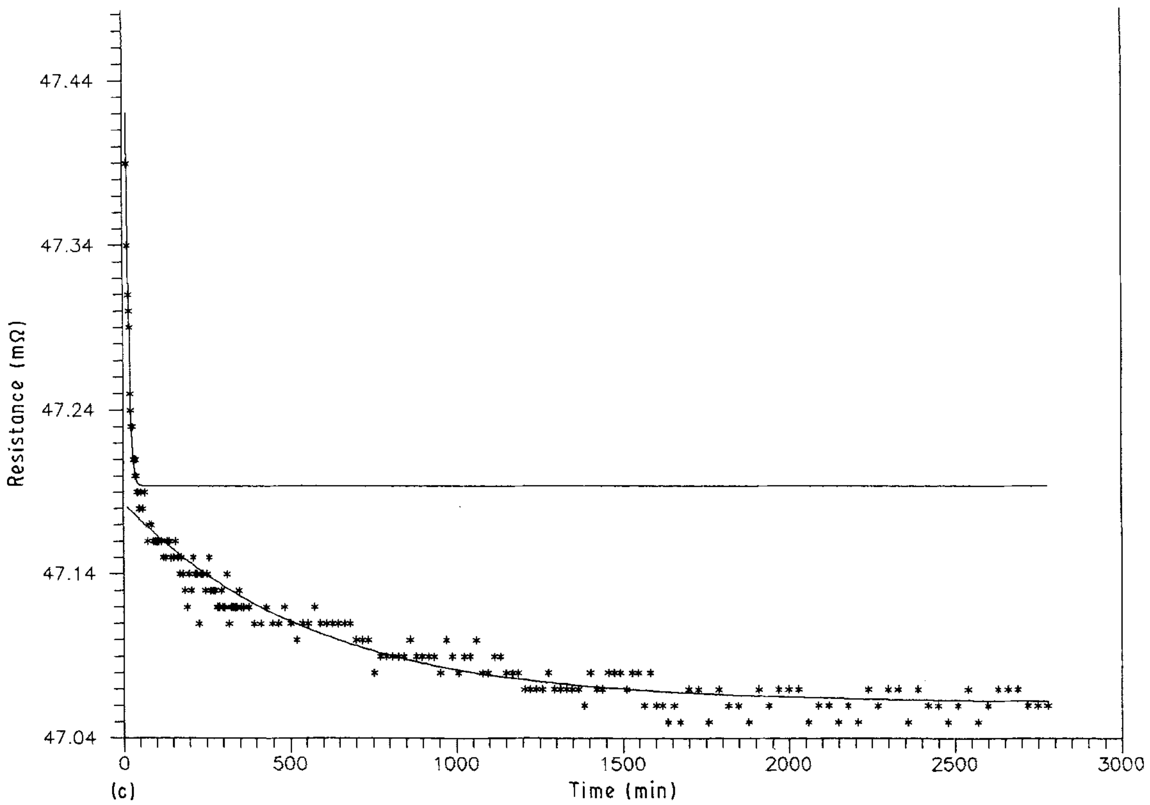

TABLE I The relevant data and fitting parameters for the resistometric isothermal curves are reported. T = Isothermal test temperature, $\langle\tau\rangle$ = average value of the relaxation times, β = standard deviation of the time distribution, α = slope of the linear "tail"; E_{A1} and E_{A2} are activation energies calculated from the Arrhenius plot when a single relaxation process can be considered ($\beta < 1.5$)

Sample	T(°C)	$\langle\tau\rangle$ (min)	Time range (min)	β	α (% h^{-1})	E_{A1} (eV)	E_{A2}
LROD	653	13.5	0–60	0.1			
	653	140.0	60–600	0.5			
	653				0.0059		
	690	9.0	0–70	0.1			
	690	126.0	70–600	0.5			
	690				0.0040		
	770	6.8	0–45	0.1			
	770	53.0	45 on	0.5			
						0.46	0.74
LROOR	653	120.0	0–470	1.0			
	653		500 on		0.0034		
	700	80.0	0–470	1.0			
	700		500 on		0.0062		
	770	30.0	0–120	3.0			
	770	190.0	120 on	0.0			
						1.00	
LRODR	650	31.0	0–120	0.0			
	650	350.0	120–1200	0.0			
	650		1200 on		0.0093		
	700	9.5	0–70	0.1			
	700	200.0	70–900	0.5			
	700		1000 on		0.0135		
	770	6.1	0–70	0.5			
	770	550.0	70 on	0.5			
						1.10	1.16

All the fitting parameters are summarized in Table I; they are explained in Section 4.

3.2. Hardness tests

Hardness tests on LROOR specimens annealed at temperatures ranging from 770–900 °C show an initial rapid softening, while recrystallization had barely begun. By contrast the curves shown in Fig. 9 illustrate the evolution of hardness of the initially disordered and cold-worked samples isothermally annealed at 500, 720, 770 and 850 °C. At the three highest temperatures the hardness increases, with respect to the preannealing value, after a few minutes of annealing.

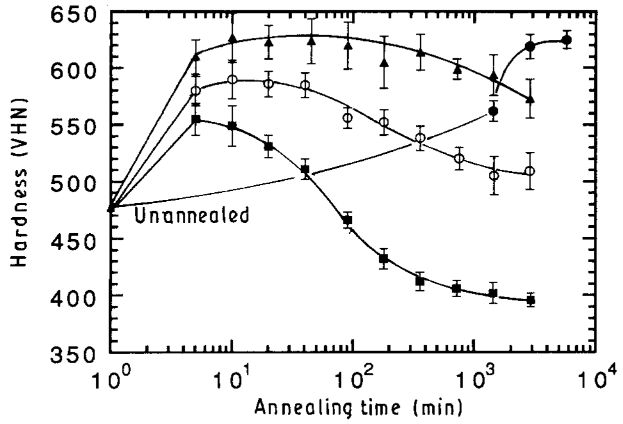

Figure 9 Microhardness of initially disordered $(Co_{0.78}Fe_{0.22})_3V$, rolled 50% and annealed at (●) 500, (▲) 720, (○) 770 and (■) 850 °C.

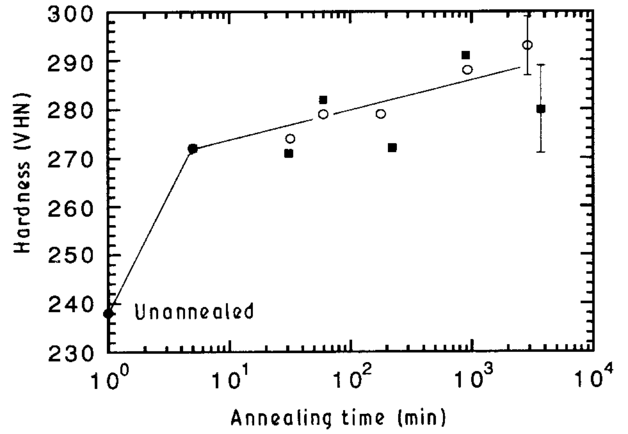

Figure 10 Hardening kinetics for initially disordered and undeformed $(Co_{0.78}Fe_{0.22})_3V$ at (○) 770 and (■) 850 °C (typical error bars are reported).

For the samples annealed at 720 and 770 °C a further increase is observed for longer times, whereas the samples annealed at 850 °C show a continuous softening. In the samples annealed at 720 and 770 °C, the hardness starts to decrease after going through a maximum value, different for the two temperatures; over the considered time range, the final hardness is still larger than that of the unannealed sample. The kinetics are, as expected, much slower at 500 °C; but, in this case too, consistent hardening can be observed after about 48 h. Some tests were also performed, for comparison, with undeformed, initially disordered alloy, annealed at 770 and 850 °C. As was to be expected from the similar ordering kinetics at these two temperatures, (see Fig. 11) the hardening kinetics were also similar, Fig. 10. Of course, the starting value of the hardness was lower than in the strained samples, and the increase was very small compared with the increase in Fig. 9. This time no maximum was observed.

3.3. X-ray diffraction analysis

The long-range order parameter was measured from the integrated intensity ratios of the superlattice reflections (1 0 0) and (1 1 0), and the fundamental ones, (2 0 0) and (2 2 0). The two available couples of reflections (superlattice and fundamental) were both considered to compensate for the possible effects of preferential orientations on the peak intensities. The variation of the long-range order parameter during isothermal annealing at three different temperatures, 720, 770 and 850 °C, of LRODR samples is shown in Fig. 11. The similarity of the kinetics at the three temperatures is due to the existence of a "nose" at about 800 °C in the *TTT* curves for reordering, that is to say some 100 °C below T_c, similar to what has been observed for several other ordering alloys. It is, moreover, worth noting that the maximum value of S is 0.8–0.9, as is to be expected, because all three selected temperatures were not far below T_c. The slight decrease of S observed after the longer anneals is likely to be due to a larger influence of extinction at higher degrees of order and lower concentration of the defects introduced, in our case, during cold-work [17]. Even though intensity data for the samples annealed at 500 °C are not available, we think, on the basis of other results, that at this temperature reordering is much slower and probably not completed even after the longer annealing times.

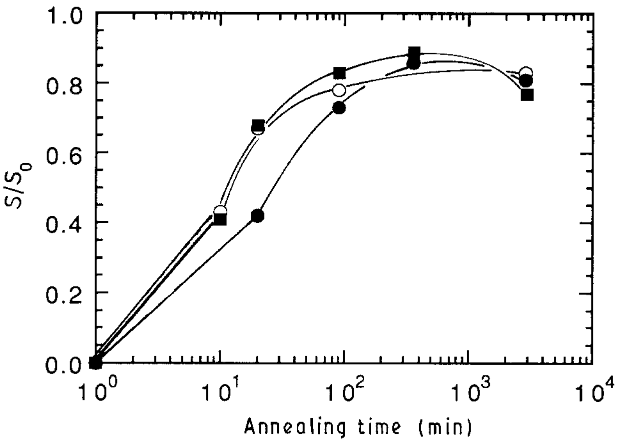

Figure 11 Increase with annealing time of the order parameter, S, at (●) 720, (○) 770 and (■) 850 °C, for initially disordered $(Co_{0.78}Fe_{0.22})_3V$, rolled 50%.

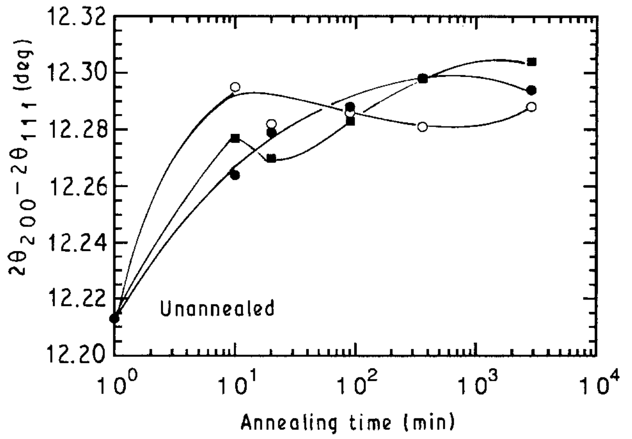

Figure 12 Increase with the annealing time of the peak separation (1 1 1)–(2 0 0), at (●) 720, (○) 770 and (■) 850 °C, for initially disordered $(Co_{0.78}Fe_{0.22})_3V$, rolled 50%.

By measuring the separation between the (1 1 1) and (2 0 0) diffraction peaks we were able to follow the recovery of the deformation faults. The increase in angular separation of the above mentioned peaks indicates a decrease in their frequency, for an fcc structure [18]. The three annealing curves of the sample LRODR, Fig. 12 show that for these deformation defects the annealing kinetics are very similar, notwithstanding the differences in the annealing temperatures.

4. Discussion

Microhardness measurements of the initially disordered alloy, rolled to 50% reduction and annealed at 720, 770 and 850 °C, show behaviour entirely different from that which was previously observed in the samples annealed after having been cold-rolled by 25% in their ordered state [10]. The hardness for the as-rolled sample is, in fact, as expected, consistently larger (580–650 VPN) for these LROOR samples, in agreement with the trend reported for other ordered alloys: larger strain-hardening when samples are deformed in the ordered state. Moreover we observed a rapid anneal-hardening followed by a plateau, at the lower temperatures (720 and 770 °C), and, in all cases, subsequent softening. In the previous study, the ordered deformed alloy shows a rapid initial softening. By comparison with the values obtained for the strain-free samples, just thermally disordered, ranging from 240 and 300 VPN, we can infer that a complete recovery and annealing out of the defects introduced by cold-rolling are not fully accomplished, even after the longer annealing times.

These observations, together with the evolution of the long-range order parameter (Fig. 11), are consistent with a position of the hardness maximum at intermediate values of S. Coherent with this picture, the initially ordered alloy, with only a very modest reduction in the degree of order caused by the 25% strain, as seen in the dilatometric tests (Fig. 5), will not show any hardening upon annealing. The positions of the hardness maxima for the originally disordered alloy (Fig. 9) are probably determined by the competition between recovery processes and progressive order-hardening. In fact, our results indicate that it is just the combined effect of reordering and annealing out of the cold-work defects that result in these hardness maxima, which are not observed in the hardness–annealing time curves relative to the undeformed samples LROD, treated at 770 and 850 °C. In these samples, in fact, only reordering occurs during the annealing and what we observe is just the small, pure order-hardening effect.

The resistometric measurements can give useful information in this regard, the electrical resistance being quite sensitive both to the degree of long-range order and to the concentration of defects. From the continuous heating curves we know about the relevant temperature ranges: these data agree with the calorimetric and dilatometric results. Particularly interesting for the study of the reordering and recovery kinetics are the isothermal tests. The variation of the state of order and of the defect configuration and concentration can all contribute to modify the potential field around each atomic site. These local inhomogeneities result in a spectrum of activation energies for the relaxation processes occurring during the anneals. Following an approach, commonly used for dealing with this kind of phenomenon (see, for a systematic treatment of the method specifically applied to resistometric measurements, [19] and references there quoted) we consider a Gaussian distribution for such activation energies. The corresponding distribution of the relaxation times is a log-normal one; the dependence of each of these on the temperature can be expressed by an Arrhenius-like relation. Accordingly, the electrical resistance, R, after a lapse of time, t, at constant temperature, T, can be written as

$$R(t,T) = R_{\mathrm{eq}}(T) + [R(0,T) - R_{\mathrm{eq}}(T)] \times \int_0^\infty \mathrm{d}\tau P(\tau)\exp(-t/\tau) \tag{1}$$

where $R_{\mathrm{eq}}(T)$ is the equilibrium value achieved by the resistance after a long annealing time, compared to the characteristic times, $R(0,T)$ is the initial value of the resistance, $P(\tau)$ is the log-normal distribution function for relaxation times

$$P(\tau) = \mathrm{const.}\exp[(\ln\tau - \ln\langle\tau\rangle)^2/\beta] \tag{2}$$

Of course the smaller is β, the standard deviation of the distribution, the closer are all the relaxation times to the average value $\langle\tau\rangle$.

The isothermal resistometric curves at the lower temperatures (650 and 700 °C) could be fitted with an exponential function followed by a linear "tail". Only exponentials were used instead for the curves at 770 °C. In all cases an initial, quite fast process was also observed, probably due to the recombination of the defects introduced by the thermomechanical disordering treatments. In agreement with the measured enthalpy outputs, the specimen LROOR, rolled 25% in the ordered state and having a very low enthalpy output, showed a first-stage recombination not so pronounced as those observed for the samples LROD and LRODR. We believe that the excess vacancies are the most active defects during this initial stage. The diffusion-controlled reordering process, too, is almost completed during the first stage of annealing, as shown by the S–annealing time curves (Fig. 11). This hypothesis is supported by the values of the apparent activation energy, which were estimated from the resistometric data when a single relaxation time could be assumed: as a rule of thumb, we assumed one single process, and so one relaxation time, to be largely predominant when $\beta < 1.5$. For larger values of β, of course, the complete spectrum of times ought to be considered. In the case of a single relaxation time, equal to the mean value of the distribution, for which we assumed an Arrhenius-like dependence on the activation energy of the process, it is possible to write

$$\langle\tau\rangle = \tau_0\exp(E_A/KT) \tag{3}$$

and consequently to evaluate τ_0 and E_A from the plot $\ln\langle\tau\rangle$ versus $1/T$. We carried out these calculations, whenever possible, being aware of the limitation of dealing with only three values of temperature. Moreover, another factor affecting our estimations is the uncertainty in the starting ($t = 0$) values of the resistance, affected by the time required for thermalizing the sample at the set temperature.

The linear relaxation stages were observed, for each series of samples, only at the lower investigated temperatures. They are most likely determined by recovery and recrystallization processes, in those samples which had been deformed, and by reordering and domain growth in the thermally disordered samples. The behaviour of the LROD samples is not very different from that of the LROOR samples, whereas the LRODR samples, with a very high deformation density, induced in the disordered state, show, after a fast starting stage, slow kinetics for longer times. These data, together with the hardness results, indicate that in the LRODR samples the high level of strain and the non-equilibrium disorder, at $T < T_c$, considerably enhance the driving force for a fast re-establishment of equilibrium, strain-free and ordered conditions. Looking at the resistometric results we can envisage a possible guideline for the comprehension of the different kinetics and obtain useful hints for the interpretation of the micrographic analysis. At 650 °C, the quickest kinetics, relative to the very first stages, is observed in the sample just thermally disordered, LROD, followed by LRODR and LROOR, in this order. As the annealing temperature is raised, there is no change in the position of the sample LROOR, whereas the other two progressively change over, and in fact, at the higher temperature (770 °C) it is the sample from the LRODR series which shows the fastest kinetics. As a tentative interpretation of these observations, we argue that as the temperature goes up, the recombination of the defects introduced during the cold-rolling plays a progressively greater role in determining reordering and recovery kinetics. Their mobility is not so high at the lower temperatures. The restoration of the long-range order, which only requires short-range diffusion, probably predominates at three low temperatures.

The enthalpy values, though affected by a certain degree of indeterminacy, because of the difficulty of estimating a precise base-line of the DSC thermograms, can be compared with the enthalpies of disordering and recrystallization, reported for other intermetallics [20], which are in the range 0.6–3.2 J g^{-1}. In agreement with these previous findings, the set of sample LROOR, 25% cold-rolled in the originally ordered conditions, gave a very low enthalpy output, too low to measure. This result proves once more that only a low degree of disorder was introduced by cold-rolling in our samples. On the other hand, the enthalpy values measured for the samples of the LROD and LRODR series were much higher. They are largely due to ordering, as also proved by the correct order of magnitude with respect to values estimated or measured for other ordered compounds. We found values of 46 J g^{-1} for series LROD, and 54 J g^{-1}, for series LRODR; both of them are comparable, for example, with the estimated value of the ordering energy for Ni_3Al, 50 J g^{-1}. We believe that the energy difference in the energy released by the LROD samples, with respect to the value obtained for the LRODR samples, can only in part be ascribed to the cold-working contribution. Isothermal measurements, presently under way, will give us more precise results.

For the LRODR samples, we have yet to explain why the recovery kinetics is so strongly dependent on the annealing temperature, as shown by the hardness tests, whereas from the resistometric and XRD results we know that the reordering rates are comparable. This will be the main aspect dealt with in Part II [11], based on micrographic observations.

Acknowledgement

This research has been supported by the EEC Science Project SCI-0262-C, "Ordering Kinetics in Alloys".

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Received 23 March
and accepted 7 April 1992