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Atomic ordering and α'-Cr phase precipitation in long-term aged Ni_3Cr and Ni_2Cr alloys

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Phase instabilities of binary Ni_2Cr and Ni_3Cr alloys after long-term exposure at temperatures between 450 and 600 °C were studied by monitoring lattice parameter, electrical resistivity and microhardness variations and by analysing the microstructural evolution of the alloys at interrupted annealing times. Both materials undergo two metallurgical changes: atomic ordering, based on the Ni_2Cr superlattice, and the precipitation of the α'-Cr phase. Short-range order develops in both alloys during the first's hours of ageing. The degree of order and kinetics of ordering transformation depend on the alloy composition, time and temperature of ageing. In Ni_2Cr, the short-range ordered structure transforms to long-range order after ageing for 100–1000 h below 525 °C, but in Ni_3Cr the transformation occurs after 30 000 h. The embrittling α'-Cr phase precipitates at grain boundaries in both alloys after long-term ageing, mainly at 550–600 °C. The amount and size of particles increase with time and temperature of ageing.

1. Introduction

The anomalies in physical properties of Ni–Cr alloys aged at temperatures below 700 °C are commonly associated with the non-random atom arrangement, in particular short-range (SRO) or long-range (LRO) order based on the formation of a Ni_2Cr superlattice. This results in a lattice contraction due to a disordered fcc matrix changing to an ordered orthorhombic phase [1–3]. SRO develops on cooling from the solution temperature and consists of a dispersion of small ordered nuclei in a disordered matrix, also known as the dispersed order state [4–6]. The degree of SRO increases during the early stages of ageing but the size of the ordered zones does not exceed the order of magnitude of a few nanometres. The peculiar feature of the resistivity increase upon ageing, also known as the *K*-state [7], is due to scattering of conduction electrons by SRO nuclei and is maximum when the size of particles is equal to the wavelength of the electrons at the Fermi level [8]. This behaviour is characteristic of all Ni–Cr alloys, with or without the addition of other alloying elements, and has been recently detected in a Ni–Cr alloy with a chromium concentration as low as 1% [9].

Ordering is a nucleation and growth type process; hence, the nucleation rate is higher at lower temperature but the growth rate, which depends on atom diffusion, increases with temperature. Moreover, the degree of order, which decreases with the test temperature, also varies markedly with chemical composition. Although coarsening of SRO nuclei is inhibited by the coherency strain between particles and matrix, in Ni_2Cr and alloys with a similar Ni:Cr atomic ratio, this structure evolves on ageing and transforms to LRO, characterized by a noticeable increment of the lattice contraction and a large negative resistivity variation [10, 11]. Ordering kinetics are relatively fast in stoichiometric Ni_2Cr alloy, where LRO forms in 100–1000 h at temperatures between 450 and 500 °C, but decreasing the chromium level of the alloy LRO kinetics become very sluggish. As a consequence, SRO was considered by several authors as the final state for Ni–Cr alloys with chromium levels up to 25 at % [12, 13].

In order to establish the ageing conditions for the possible occurrence of the SRO–LRO transition in Ni_3Cr alloy, which is representative of a large number of commercial materials with a similar Ni:Cr ratio, samples of this alloy were subjected to isothermal treatments in the 450–600 °C temperature range for up to 30 000 h ageing. The ordering behaviour was inferred by measuring lattice contractions by X-ray diffraction as well as electrical resistivity and microhardness variations upon ageing at different temperatures. The microstructural evolution of the alloy at each temperature was examined by electron microscopy techniques, while a parallel study was conducted on Ni_2Cr alloy.

2. Materials and experimental details

Experimental melts of Ni_3Cr (Ni–25 at % Cr) and Ni_2Cr (Ni–33 at % Cr) were cast and hot extruded to 15 mm diameter bar. Samples of both alloys were pre-treated at 1080 °C, 4 h, air coded, +700 °C, 16 h, air coded, and then subjected to isothermal ageing treatments at 450, 475, 500, 525, 550 and 600 °C for up to 30 000 h, followed by water quenching.

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Lattice parameter variations upon ageing were determined by X-ray diffraction, using the CuK_α radiation at the constant temperature of 29 ± 1 °C. Sample surfaces, carefully polished and then electropolished to avoid work-hardening effects, were rotated perpendicular to the beam direction to improve the resolution. The shifting of position of the 331 reflection peak, occurring at an angle 2θ of about 140 °C, was measured.

High-precision d.c. resistance measurements were performed at −196 °C on each sample prior to any ageing and then at interrupted annealing times, using the conventional four-terminal potentiometric method with a current of 0.5 A passed through the sample and then reversed to avoid thermal e.m.f.s. Voltage drops were measured with a resolution of 10 μV.

Microhardness (0.98 N, 30 s) measurements were performed on the same sample surfaces previously prepared for the X-ray diffraction.

The microstructural evolution of the alloys during ageing at different temperatures was examined by scanning (SEM) and transmission (TEM) electron microscopy. Sample surfaces, previously used for X-ray diffraction, were etched in a solution of 10 ml HF + 100 ml HNO_3 for 30–240 s, before SEM examination. Thin-foil techniques were used on 3 mm diameter discs, thinned in a solution of 10% perchloric acid in methanol at the temperature of −30 °C. Particle compositions were determined, when possible, by STEM microanalysis.

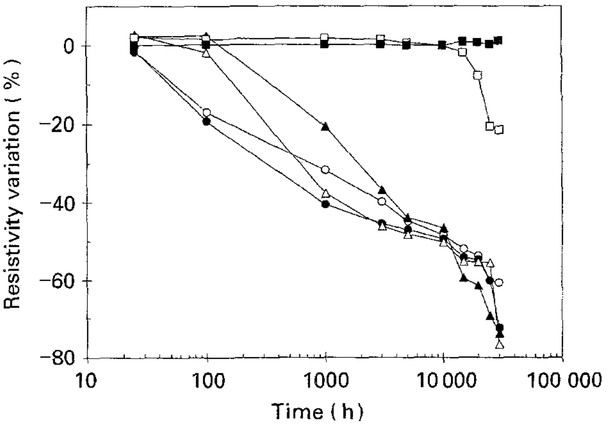

Figure 1 SRO- and LRO-induced resistivity variations upon ageing in Ni_2Cr at (○) 450 °C, (●) 475 °C, (△) 500 °C, (▲) 525 °C, (□) 550 °C, (■) 600 °C.

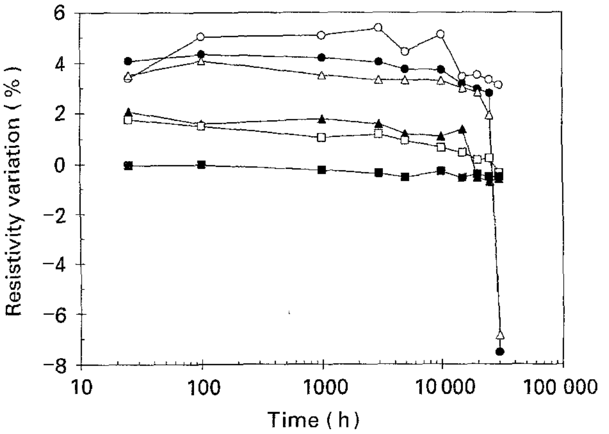

Figure 2 SRO- and LRO-induced resistivity variations upon ageing in Ni_3Cr at various temperatures; for Key, see Fig. 1.

3. Results and discussion

3.1. Effects of short- and long-range order on physical properties

At each temperature, the isothermal resistivity variations of Ni_2Cr (Fig. 1) and Ni_3Cr (Fig. 2) were first characterized by an increment, occurring during the initial stages of ageing, followed by a plateau. In both alloys, the magnitude of maximum increment, corresponding to the degree of SRO of the alloy at the given temperature, decreases with increasing temperature, according to the classical theory of nucleation and growth of precipitates [14, 15]. It follows that a large number of SRO nuclei of a smaller size induces a larger resistivity increment than a lesser quantity of coarse-ordered zones. Furthermore, the SRO-induced resistivity variations of Ni_3Cr are larger as compared to those of Ni_2Cr alloy subjected to the same treatments, e.g. after 24 h ageing at 500 °C resistivity increments of 2.8% in Ni_2Cr and of 3.5% in Ni_3Cr were measured. This behaviour led early authors to assume simply the formation of an ordered phase with Ni_3Cr composition [16]. It must be pointed out that the lattice parameter decreases with increasing nickel concentration [17] and, in particular, the lattice parameters of pre-treated Ni_3Cr and Ni_2Cr were measured to be 0.355 53 and 0.356 81 nm, respectively. As a consequence, the larger resistivity increment measured in Ni_3Cr as compared to Ni_2Cr is attributable to the increased coherency strain between ordered particles and matrix and, as a consequence, to the enhancement of the factor of electron scattering by SRO nuclei with decreasing atomic density of the matrix.

On prolonged ageing, the resistivity of Ni_2Cr decreases sharply, after stages of stability of different duration depending on temperature, in particular less than 24 h at 450 and 475 °C, 100 h at 500 °C, 1000 h at 525 °C and 15 000 h at 550 °C. The sudden resistivity reduction occurs when the dimensions of ordered domains exceed the critical size and hence it is attributed to the formation of LRO. Resistivity minima may be correlated to the degree of LRO of the alloy at a given temperature. The larger degree of LRO of Ni_2Cr was measured after 30 000 h at 500 °C, corresponding to a resistivity variation of −76%.

On the contrary, in Ni_3Cr, the values of the SRO-induced resistivity increments remain in equilibrium for at least 25 000 h ageing at all temperatures, confirming that such a structure is stable for a very long time, but further ageing between 25 000 and 30 000 h in the 475–525 °C temperature range results in a resistivity drop of −7%, which finally indicates the onset of LRO also in the off-stoichiometric alloy.

Although the X-ray diffraction failed to provide any evidence for the ordered Ni_2Cr phase, due to the similarity of the atomic scattering factors of nickel and chromium, however, lattice parameter variations upon ageing at different temperatures indicate that

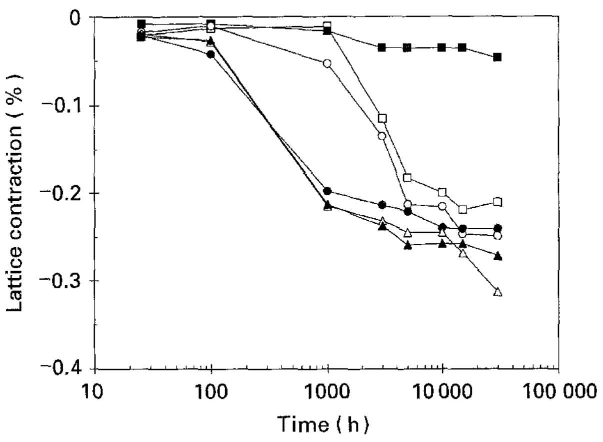

Figure 3 SRO- and LRO-induced lattice contraction in Ni_2Cr at various temperatures; for Key, see Fig. 1.

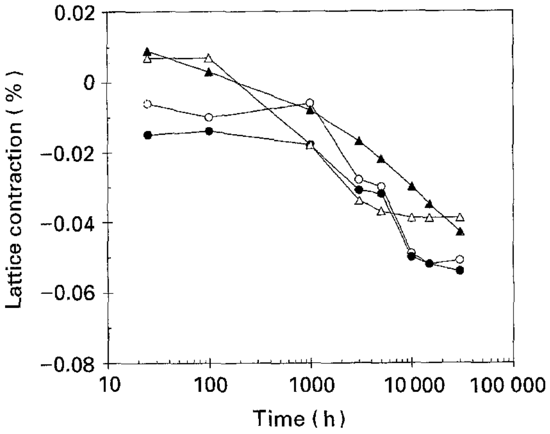

Figure 4 SRO- and LRO-induced lattice contraction in Ni_3Cr at various temperatures; for Key, see Fig. 1.

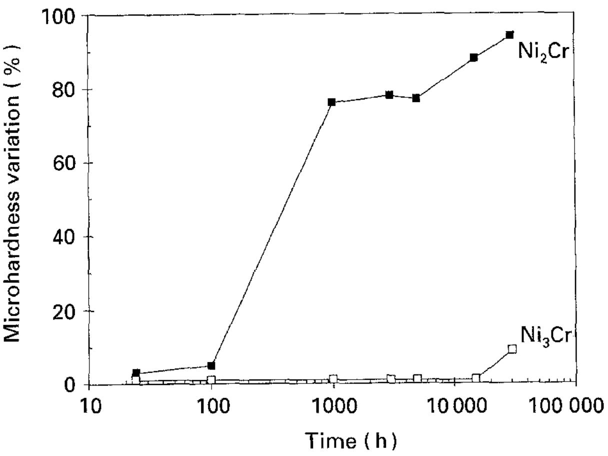

Figure 5 LRO-hardening upon ageing at 475 °C in (■) Ni_2Cr and (□) Ni_3Cr.

both alloys contract during isothermal treatments below 550 °C. Limited lattice contraction accompanying SRO markedly increases due to LRO formation, but the extents of contractions greatly differ, and lattice variations, reaching an order of magnitude of −0.3% in Ni_2Cr (Fig. 3), do not exceed the value of −0.06% in Ni_3Cr (Fig. 4) after 30 000 h ageing at 525 °C and below. At 550 °C, the lattice of Ni_2Cr contracts after ageing for 1000–3000 h and indicates long-range ordering.

It should be noted that the lattice contraction in Ni_2Cr occurs in three stages: (i) slightly and slowly during the initial stages of isothermal treatments, when the alloy is short-range ordering and the degree of SRO is increasing, (ii) rapidly during the SRO–LRO transition, and (iii) slowly again when the alloy is fully long-range ordered but the dimensions of domains, and hence the degree of LRO, are still increasing. Furthermore, the second stage of contraction is characterized by a gradual broadening of the diffraction peaks [17]. This effect, which suddenly vanishes when the alloy reaches the third stage of contraction, was also observed by other authors [18]. It can be attributed to the coexistence of zones with different degrees of order, in that a certain degree of SRO exists after cooling from solution treatment but subsequent annealing produces fresh SRO nuclei and hence the previously nucleated zones acquire a degree of LRO earlier than the just nucleated zones.

In both alloys the magnitude and kinetics of lattice contractions are usually in good agreement with those of resistivity variations, but there is an apparent discrepancy between the kinetics of resistivity variation and of lattice contraction of Ni_2Cr aged at 550 °C. This can be interpreted as due to the reduced number of ordered zones which nucleate at this temperature and hence produce a smaller resistivity increment as compared to lower temperatures, but, once nucleated, these particles grow rapidly and cause a noticeable lattice contraction after a relatively short ageing time, i.e. 1000 h, while the resistivity decreases after 15 000 h only.

During ageing at 475 °C, the microhardness of Ni_2Cr increases markedly between 100 and 1000 h ageing and then continues to increase slowly reaching a 94% increment in 30 000 h (Fig. 5). On the contrary, no significant microhardness variations occur in Ni_3Cr aged for at least 15 000 h at the same temperature, but a 9% increment was measured after 30 000 h ageing.

The concomitance between microhardness rise and resistivity drop together with sharp lattice contraction leads to the conclusion that the main factor in hardening is the degree of LRO, as observed by other authors [19]. On the contrary, this property is almost insensitive to the existence of a SRO structure and this is in agreement with previous studies on some nickel-based superalloys, which showed that SRO causes a sensible increase of hardness only in the presence of a high dislocation density [20].

3.2. Microstructural observation of ordered alloys

The microstructural evolution of the ordered Ni_2Cr phase in both binary alloys correlates well with the variations of physical properties, but it must be pointed out that, while the LRO structures can be unambiguously identified by TEM analysis, the examination of SRO structures always requires very careful interpretation.

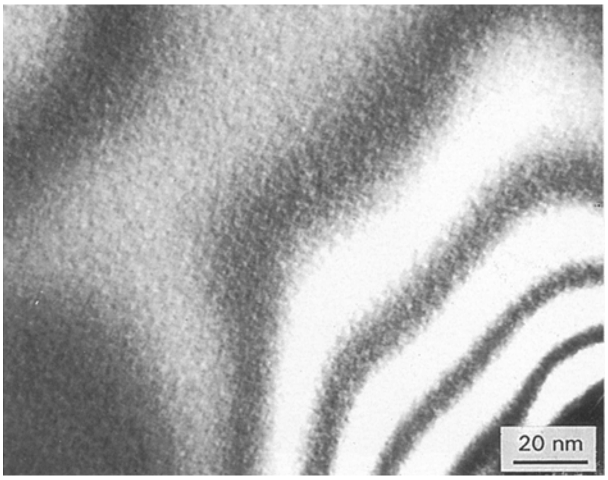

Figure 6 Mottled contrast characteristic of SRO in Ni_2Cr, 500 °C, 500 h, water quenched.

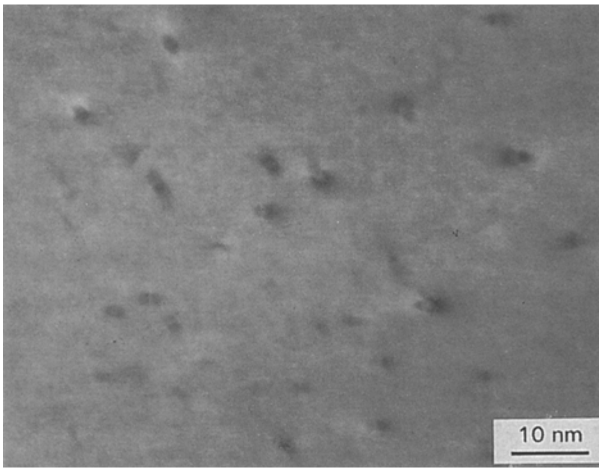

Figure 7 LRO embryos in Ni_2Cr, 550 °C, 1000 h, water quenched.

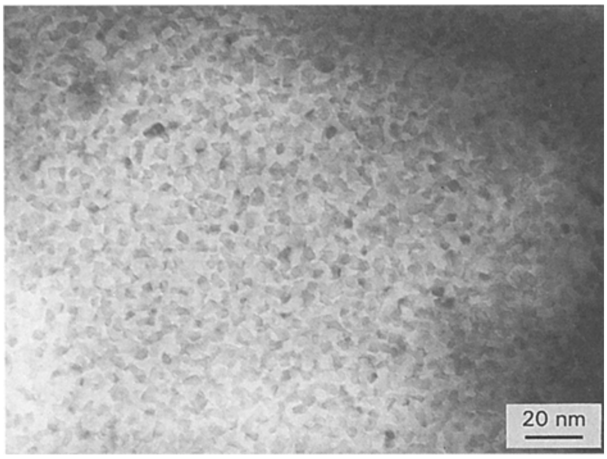

Figure 8 LRO structure of Ni_3Cr, 500 °C, 30 000 h, water quenched.

Thin-foil microscopy observation of both solution-treated materials revealed mottled contrast (Fig. 6). This effect, previously attributed to SRO [21, 22], is considered to arise from the interaction of weak localized strain fields caused by the homogeneous precipitation of ordered nuclei, which are too small to be resolved individually. This kind of contrast appears enhanced by ageing, consistent with the assumption of an increasing degree of SRO; nevertheless, some factor other than SRO is considered to give rise to mottled contrast, because it was observed to persist in well-established LRO domains of Ni_2Cr [10]

Selected-area diffraction patterns (SADP) of both short-range ordered alloys are characterized by diffuse scattering [23–25]. Streaking of fundamental reflections in $\langle 1\,1\,0 \rangle$ direction indicates strain in the $\{1\,1\,0\}$ family of planes, consistent with the orientation relationship between the matrix and the ordered phase [2]; nevertheless, diffuse scattering does not unambiguously characterize SRO too, because it was observed, for example, in diffraction patterns of pure nickel arising from the double diffraction of NiO rings [26].

In conclusion, although the phenomena of mottled contrast and diffuse scattering in the Ni–Cr system cannot be considered proof of SRO in themselves, in the case of Ni_2Cr they are always observed whether in short-term aged samples or in samples long-term aged at higher temperatures, i.e. when the results of lattice parameter, resistivity and microhardness measurements suggest that the alloy is in the SRO state.

The microstructure of long-range ordered Ni_2Cr reveals both homogeneous and heterogeneous nucleation of ordered domains [10]: (i) at 450–525 °C, where the degree of supersaturation is large, uniformly distributed LRO domains were observed after 1000 h ageing and were identified by superlattice reflections in diffraction patterns. Ordering proceeds by growth of domains until the fields of influence associated with particles begin to impinge on each other, then only a slight coarsening occurs. Superlattice reflections become stronger with increasing ageing time, confirming the establishment of LRO and the increase of the degree of LRO upon ageing. Data in the literature support the findings that in this temperature range the LRO domains attain a size of the order of some tens of nanometres and that the subsequent growth is very sluggish [2, 3, 12, 21]; (ii) at 550 °C, the homogeneous nucleation is difficult because of the low degree of supersaturation and hence the nucleation of ordered domains is heterogeneous. In particular, a few small features were made visible by bright/dark lobe contrast in the sample treated for 1000 h (Fig. 7). Those LRO embryos grow rapidly on ageing and, after 2500 h, isolated coherent ordered domains of some thousands of nanometres appear to have nucleated on the defects. Faint superlattice reflections are visible only after ageing for 10 000 h.

Mottled contrast and diffuse scattering typical of the SRO state characterize the microstructure of Ni_3Cr for very long ageing times at all temperatures. Very small coherent particles were imaged by matrix strain contrast after ageing for 10 000 h at 475–525 °C, providing direct evidence of the dispersed ordered state [10]. Uniformly distributed LRO domains appear after 30 000 h at 500–525 °C (Fig. 8), but the dimensions of the domains (~ 5 nm) are very small, compared to those of Ni_2Cr (Fig. 9) after corresponding treatments (20–50 nm). Superlattice reflections are

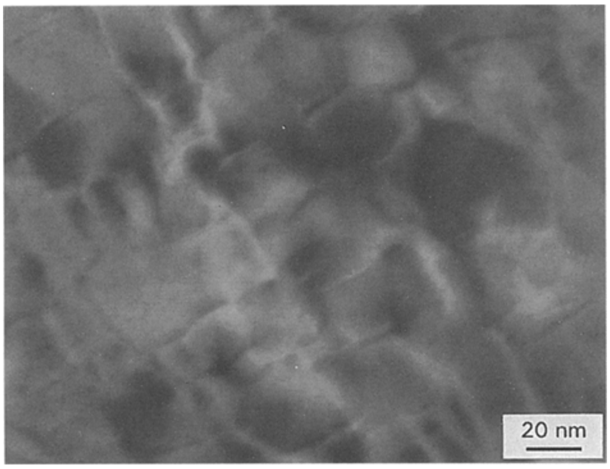

Figure 9 LRO structure of Ni_2Cr, 500 °C, 30 000 h, water quenched.

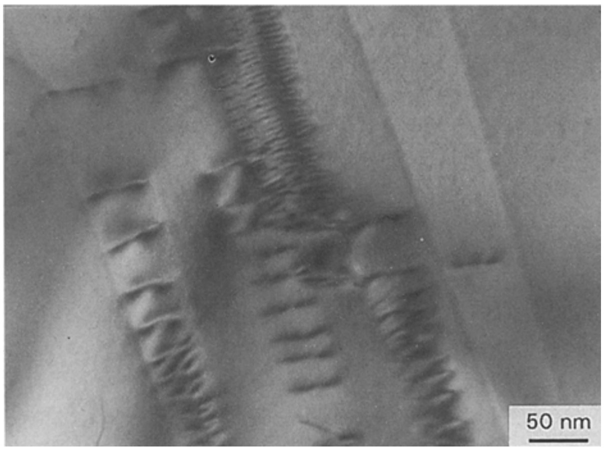

Figure 11 Pile-ups of dislocations in Ni_2Cr, 600 °C, 30 000 h, water-quenched.

not visible, but this can be reasonably attributed to the fact that dimensions of the ordered zones in Ni_3Cr after 30 000 h are of the same order of magnitude as those of Ni_2Cr after 100 h, and that the diffraction patterns of Ni_2Cr under these conditions only showed diffuse scattering too.

It is known that ordering alters the mechanical properties by affecting the dislocation morphology: pile-ups of dislocations in the absence of evident obstacles often form, because one dislocation moving along a particular slip plane destroys SRO across the plane and thus facilitates glide of successive dislocations on the same plane [27, 28]. When the alloy possesses a high degree of SRO or a low degree of LRO, i.e. when the ordered domains are smaller than the width of the antiphase boundaries between pairs of superdislocations, unusually long dislocation pile-ups form. Fig. 10 shows an ~ 1 μm long dislocation pile-up in Ni_3Cr aged for 30 000 h at 500 °C. It should be noted that such dislocation arrays were not seen in Ni_2Cr after the same treatment, due to the higher degree of LRO of the stoichiometric alloy, but they were observed whether after shorter ageing at the same temperature or after the same ageing time at 600 °C (Fig. 11). It must be pointed out that an applied stress greatly enhances the formation of dislocation pile-ups and that sudden release of dislocation arrays results in serrated flow during mechanical tests, strain

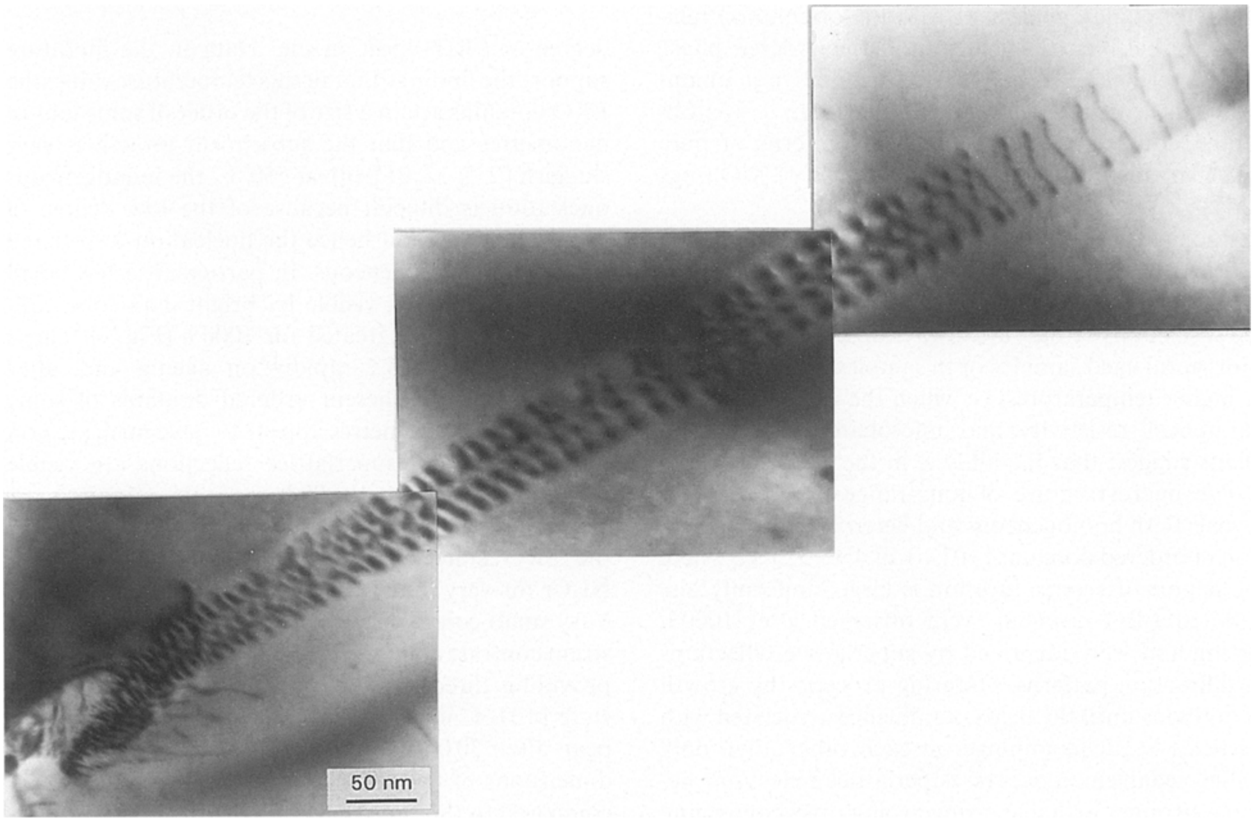

Figure 10 Pile-up of dislocations in Ni_3Cr, 500 °C, 30 000 h, water quenched.

bursts during creep, and can nucleate cracks at grain boundaries unable to accommodate sudden avalanches of dislocations [10].

3.3. Precipitation of the α′-Cr phase

Microstructural examination of both long-term aged alloys revealed the presence of precipitates at grain boundaries, initially at triple points (Figs 12 and 13). The composition of those particles was determined, when possible, by STEM microanalysis: the chromium concentration was evaluated to range from 80%–97%, corresponding to the composition of the embrittling α′-Cr phase. The b c c structure of precipitates was confirmed by the analysis of SADP. The precipitation kinetics is very slow and depends on temperature: a few very small particles were observed after ageing for 10 000 h or more below 550 °C, but the amount and size of particles noticeably increase with temperature of ageing and, after 30 000 h at 600 °C, the precipitates can attain the order of magnitude of some micrometres. This results in an appreciable widening of grain boundaries, which is known to cause embrittlement [29], in both alloys.

Numerous annealing twin boundaries form in Ni_2Cr after long-term ageing at 550–600 °C, which appear filled by precipitates (Fig. 14). The α′ particles located at twins boundaries are generally smaller in size, as compared to those precipitated at grain boundaries, probably due to the later nucleation. It should be noted that very little twinning occurs in Ni_3Cr after similar ageing conditions.

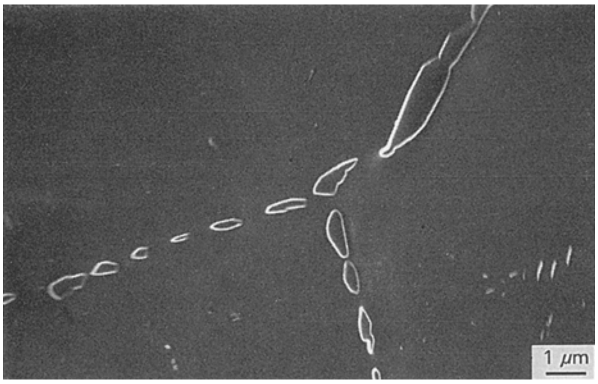

Figure 12 α′ particles at grain boundaries of Ni_3Cr, 600 °C, 30 000 h, water quenched.

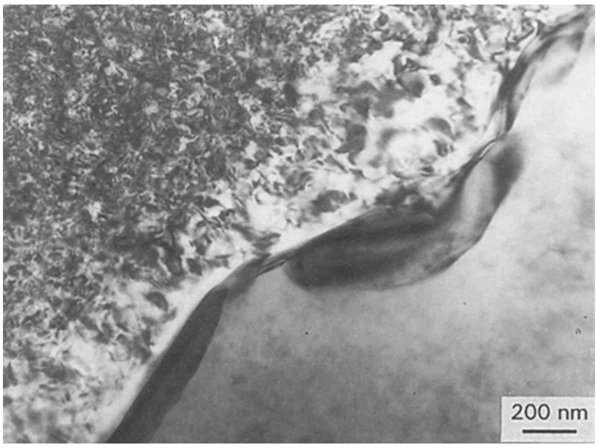

Figure 13 α′ particles at a grain boundary of Ni_2Cr, 600 °C, 30 000 h, water quenched.

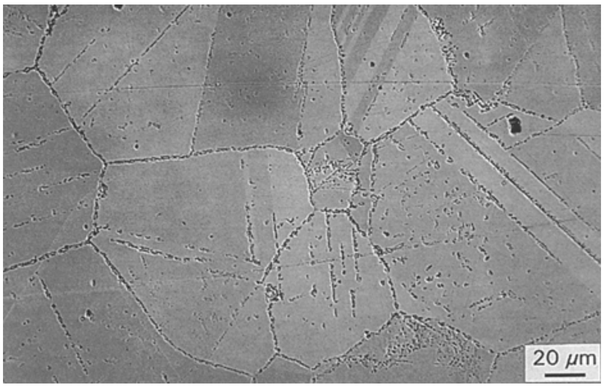

Figure 14 α′ phase at grain and twin boundaries of Ni_2Cr, 600 °C, 30 000 h, water quenched.

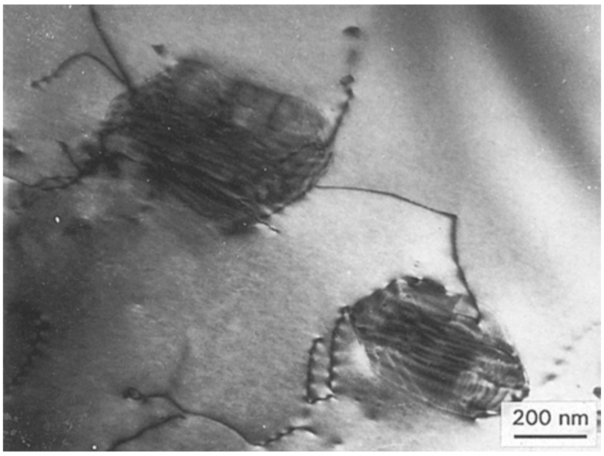

Figure 15 α′ particles in grains of Ni_3Cr, 600 °C, 30 000 h, water quenched.

Finally, further increment of the α′ precipitation does not result in an indefinite growth of particles at grain boundaries but groups of large particles, often with dislocations noticeably decorated, are observed in grains (Fig. 15). The α′ particles are obstacles to glide of dislocation arrays which form on ordering, hence the regions neighbouring the α′ precipitates appear to be preferred sites for dislocation pile-ups. This may also contribute to the embrittlement of the alloys.

4. Conclusion

Both Ni_2Cr and Ni_3Cr alloys undergo an ordering transformation based on the Ni_2Cr superlattice. SRO kinetics are very similar in both alloys: SRO develops after solution treatment and during the early stages of ageing, accompanied by a significant resistivity increment and limited lattice contraction. The degree of SRO, which corresponds to maximum resistivity variation, decreases with increasing temperature and is higher in Ni_3Cr due to the higher nickel concentration.

On prolonged ageing, LRO forms, accompanied by sharp resistivity decrease, lattice shrinkage and microhardness increase. The degree of LRO depends on chromium concentration and hence is much smaller in Ni_3Cr as compared to Ni_2Cr after the same treatment. LRO kinetics depends on the alloy composition and ageing condition: LRO develops after ageing for 100–1000 h at 450–525 °C in Ni_2Cr (ageing time increases with temperature) but it takes 30 000 h to form Ni_3Cr. Moreover, Ni_2Cr possess an LRO structure after ageing for 15 000 h at 550 °C, whereas at this temperature, Ni_3Cr is short-range ordered up to the duration of the experiments.

Microstructural examination of SRO structures revealed mottled contrast, accompanied by diffuse scattering in diffraction patterns, whereas homogeneous or heterogeneous distribution of ordered domains, accompanied by Ni_2Cr superlattice reflections in diffraction patterns, characterize LRO structures. The amount and size of domains depend on time and temperature of ageing. The size of ordered domains observed in Ni_3Cr aged for 30 000 h at 500–525 °C is much smaller as compared to that of Ni_2Cr after the same treatments.

The α'-Cr phase precipitates in both alloys after long-term ageing, mainly at 550–600 °C. The amount and size of particles, as well as their distribution, depend on time and temperature of ageing.

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