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A study of the effects of phosphorus content, cold rolling and heat treatment on the kinetics of ordering in Ni_2Cr alloys

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Three Ni_2Cr alloys, with phosphorus contents of 0.002, 0.017 and 0.078 wt%, were prepared as cast slabs, which were then thermomechanically treated by four different schedules to a final thickness 0.38 mm. The isothermal ordering kinetics of the Ni_2Cr alloys was investigated in specimens aged at 450, 500 and 550° C for times ranging from 2 h to 40 days, by surface hardness measurements and microstructural investigation. It was found that increasing the phosphorus content from 0.002 to 0.078 wt% causes a significant increase in the rate of the order transformation in those materials which were annealed at 900° C for 1 h followed by water quenching. Also cold rolling the Ni_2Cr alloys by 6,12 and 21% reduction in thickness was found to completely eliminate the effect of the phosphorus on the rate of the order transformation, for the medium and high phosphorus content materials, whereas for the low phosphorus content (0.002 wt%) material, cold rolling was found to increase the rate order transformation compared to that of the annealed structure.

1. Introduction

The nickel–chrome superalloys are designed for applications where corrosion, oxidation resistance and high strength properties are required. However, cold working to achieve higher strength makes them susceptible to hydrogen embrittlement. This susceptibility has been linked to the segregation of impurities such as phosphorus and sulphur to grain boundaries [1–3].

Ni_2Cr is an alloy which is often used as a model material for fundamental studies of the properties of the nickel-based superalloys, since it undergoes a similar slow long-range order (LRO) transformation. It has been reported by several authors [4–6], that on cooling below a critical temperature T_c of about 950° C, Ni_2Cr transforms from a disordered face centred cubic structure to a body centred orthorhombic superlattice.

Recently, Lehman and Kosel [7] investigated the isothermal ordering kinetics of Ni_2Cr alloys, with three phosphorus levels, aged at 500° C and found that the high phosphorus specimens transformed much faster than the lower phosphorus containing alloys. The middle and low phosphorus materials were found to transform by a continuous ordering process. Whereas, the high phosphorus specimens transformed by an unusual process in which colonies of ordered domains were formed which consumed grains through the advance of an order–disorder interface.

The order–disorder transformation in this material has been studied by a number of different techniques such as surface hardness measurement [5], volume changes [5, 8], electrical conductivity [5, 9], X-ray diffraction [7, 8] and transmission electron microscopy [7].

The purpose of the present study was to obtain a more detailed understanding of the effects of phosphorus and thermochemical treatment on the kinetics of the order–disorder transformation in Ni_2Cr. Changes in surface hardness and metallography were used to measure the degree of ordering and study the kinetics of the transformation.

2. Material and experimental procedure

Three Ni_2Cr alloys, with phosphorus levels of 0.002, 0.017 and 0.078 wt % were prepared as cast slabs by the Cabot Corporation (Kokomo, Indiana, USA). The chemical compositions of the alloys are given in Table I.

The three alloys were thermomechanically processed to obtain material of final thickness 0.38 mm by the following four schedules:

(a) Alternately cold rolling and annealing at 1150° C in an inert gas atmosphere followed by water quenching until the final thickness was achieved. This material was then annealed at 900° C for 1 h followed by water quenching.

(b) Cold rolling and annealing to a thickness of 0.40 mm, followed by cold rolling to the final thickness (6% plastic deformation).

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TABLE I Chemical compositions of Ni_2Cr model alloys

Heat no.	C	Cr	Mn	Mo	N	Ni	P	S	Si	W
9480	0.015	31.02	0.01	0.01	0.004	68.17	0.002	0.002	0.01	0.01
9580	0.015	30.55	0.01	0.02	0.005	67.27	0.017	0.003	0.01	0.04
9680	0.008	30.56	0.01	0.01	0.004	68.87	0.078	0.002	0.05	0.14

(c) Cold rolling and annealing to a thickness of 0.43 mm, followed by cold rolling to the final thickness (12% plastic deformation).

(d) Cold rolling and annealing to a thickness of 0.48 mm, followed by cold rolling to the final thickness (21% plastic deformation).

Samples from each of the thermomechanical processing schedules were aged at temperatures of 450, 500 and 550° C (± 5° C) for times ranging from 2 h to 40 days. Surface hardness measurements and microstructural observations were used to determine the degree of order–disorder transformation. Hardness testing was done on a Leco M-400 hardness tester using a Knoop indenter with a load of 200 g. The average of ten hardness measurements was taken for each of the heat treatment conditions. The accuracy of the measurements was ± 10 Knoop hardness (KH).

3. Results

3.1. Effect of phosphorus content on the kinetics of order–disorder transformation

The effects of phosphorus content and ageing temperature on the kinetics of the order–disorder transformation were studied in material which was solution annealed at 900° C followed by water quenching. Figs 1 and 2 show the change in surface hardness as a function of ageing time at temperatures of 450 and 500° C, respectively, for the three different phosphorus level materials. At 450° C ageing temperature, complete transformation occurred in the high phosphorus material (0.078 wt %) after about 2 days, whereas for the medium (0.017 wt %) and low (0.002 wt %) phosphorus materials, 20 and > 36 days were required, respectively. At 500° C complete transformation occurred sooner: 10 h for the high phosphorus, 10 days for the medium phosphorus and 12 days for the high phosphorus materials, respectively. At 550° C however, no transformation was observed in any of the materials even after 40 days ageing.

Fig. 3 shows a typical microstructure of a low phosphorus (0.002 wt %) sample which was aged for 12 days at 500° C. Under these heat treatment conditions, the mean grain size is 65 μm and the matrix is completely transformed to the ordered state. Figs 4 to 6 show typical microstructures for samples of the high phosphorus (0.078 wt %) material aged at 450° C for 10 h, 5 days and 12 days, respectively. Similarly, Figs 7 to 9 show typical microstructures for the high phosphorus (0.078 wt %) material aged at 500° C. The grain size obtained by ageing at 450° C is much finer than that produced by ageing at 500° C as shown in Table II. This may be due to a higher rate of nucleation of the ordered domains at 450° C, which leads to a finer grain size of the ordered phase.

3.2. Effect of cold rolling and phosphorus content on the kinetics of the order–disorder transformation

The kinetics of the order–disorder transformation in materials with three different phosphorus contents (0.002, 0.017 and 0.078%), cold rolled 6, 12 and 21% reduction in thickness, were studied at 450, 500 and 550° C by using change in surface hardness as an indication of the degree of transformation.

Figs 10 to 12, show the surface hardness as a function of ageing time at 500° C for the three phosphorus content materials cold rolled 6, 12 and 21%, respectively. For the low (0.002%) phosphorus content material, complete ordering is obtained after about 10 days ageing, independent of the amount of cold rolling. However, for the medium (0.017%) and high (0.078%) phosphorus content materials, there was a slight dependence on the amount of prior cold rolling, with the time required for complete ordering, decreasing from about 10 days for the 6% cold rolled, to 8 days for the 21% cold rolled materials, respectively.

Table III shows the time for complete ordering, for the three phosphorus content materials, in the solution annealed and cold rolled conditions, aged at 450 and

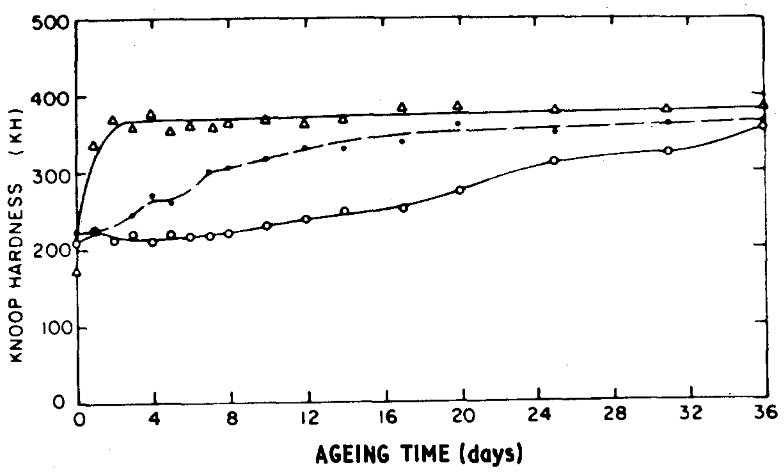

Figure 1 The progress of the order–disorder phase transformation measured by surface hardness increase. Solution annealed at 900° C, aged at 450° C. (△) 0.078 wt % phosphorus, (●) 0.017 wt % phosphorus, (○) 0.002 wt % phosphorus.

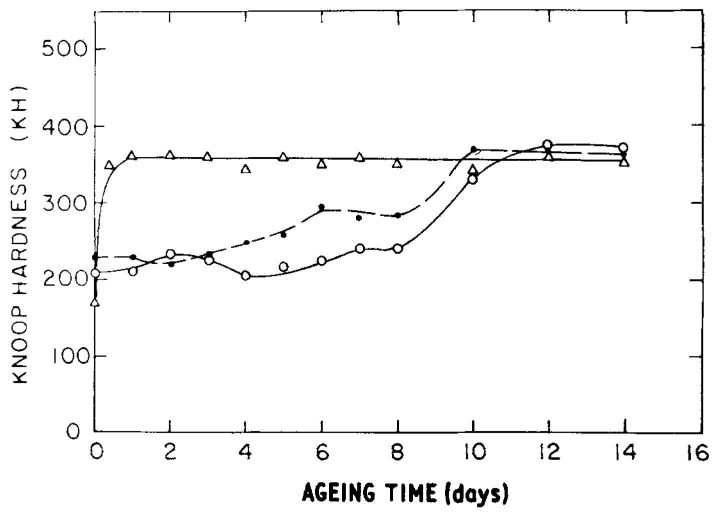

Figure 2 The progress of the order–disorder phase transformation measured by surface hardness increase. Solution annealed at 900° C, aged at 500° C. (△) 0.078 wt % phosphorus, (●) 0.017 wt % phosphorus, (○) 0.002 at % phosphorus.

500° C. There was a significant effect of phosphorus, on the time for complete ordering, in the solution annealed material, at both ageing temperatures. At 450° C changing the phosphorus content from high (0.078%) to low (0.002%) caused an increase in the time for complete ordering from about 2 days to greater than 36 days. Whereas, at 500° C ageing temperature, complete ordering occurred much more rapidly, requiring only 10 h and 12 days for the high and low phosphorus materials, respectively.

Cold rolling 21% prior to ageing at 450° C caused an increase in the time for complete ordering from about 8 days for the high phosphorus to 28 days for the low phosphorus materials. In the material cold rolled 6% prior to ageing at 500° C, 10 days were required for complete ordering, and no effect of phosphorus content was observed. Cold rolling 12 and 21% prior to ageing at 500° C, resulted in a slight effect of the effect of phosphorus, with the time for complete ordering increasing from 8 to 10 days for the high and low phosphorus materials, respectively.

4. Discussion

4.1. Effect of ageing temperature and phosphorus content on the kinetics of order–disorder transformation

The formation of a superlattice from a disordered solid solution is now recognized thermodynamically to be a first order transformation which may occur by nucleation and growth processes. Provided that both the initial and final structures are both single phases, the ordering process may involve atomic rearrangements without the need for long-range diffusion [10]. The nucleation rate for the order–disorder transformation can be increased considerably by increasing the driving force for the transformation, by increasing the degree of undercooling below T_c (critical temperature for the order–disorder transformation). The growth rate, being controlled by an activation energy which is nearly temperature independent, decreases as the ageing temperature decreases.

Ageing at 550° C, which is only just below T_c [8], produces only a small driving force, which is insufficient for the formation of supercritical nuclei. Thus, the transformation does not occur, even after 40 days ageing. Decreasing the ageing temperature to 500° C increases the driving force considerably, which results in the formation of supercritical nuclei. Also, under these conditions, the growth rate of the nuclei is high, thus the order–disorder transformation rate is close to its maximum value. On further decreasing the ageing temperature to 450° C, the rate of nucleation is increased still further, due to increased undercooling, however, the rate of growth decreases, which results in an overall slower rate of transformation (Table II). This results in a finer grain size being produced by ageing at 450° C (Fig. 5), compared to that produced by ageing at 500° C (Fig. 8).

In agreement with the results of Lehman and Kosel. [7], the phosphorus content was found to have a considerable effect on the rate of the order–disorder transformation in material which was aged, after

TABLE II Average grain size of Ni_2Cr as a function of ageing temperature and time

Ageing temperature (° C)	Ageing time	Transformation	Grain size (μm)
450	10 h	incomplete	22
	5 days	complete	22
	12 days	complete	45
500	10 h	complete	65
	5 days	complete	90
	12 days	complete	90

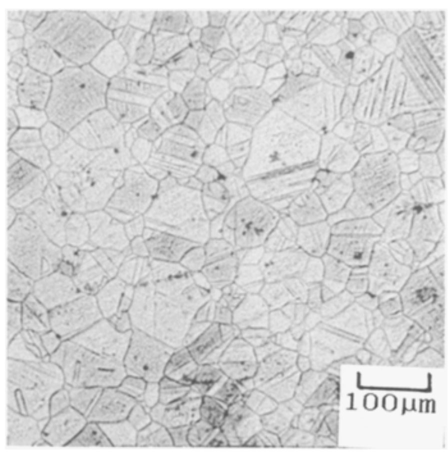

Figure 3 Microstructure of low phosphorus material solution annealed at 900° C, aged at 500° C for 288 h.

TABLE III Effect of cold rolling and phosphorus content on the time for complete order transformation

Ageing temperature (° C)	Cold rolling	Time for complete ordering		
		Low phosphorus	Medium phosphorus	High phosphorus
450	Solution annealed	> 36 days	20 days	2 days
	21%	28 days	14 days	8 days
500	Solution annealed	12 days	10 days	10 hrs
	6%	10 days	10 days	10 days
	12%	10 days	8 days	8 days
	21%	10 days	8 days	8 days

solution annealing at 900° C for 1 h followed by water quenching. From the present results it was found that, in material aged at 500 and 450° C, increasing the phosphorus content, from low (0.002 wt %) to medium (0.017 wt %), reduced the time for complete ordering by 16 and 44%, respectively. Similarly, increasing the phosphorus content from low (0.002 wt %) to high (0.078 wt %) reduced the time for complete ordering by 96 and 94%, at ageing temperatures of 500 and 450° C, respectively.

Lehman and Kosel [7] concluded from X-ray, transmission electron microscopy, and metallography studies that, for the low and medium phosphorus materials, a continuous ordering mechanism was active, which produced a relatively uniform domain size within the grains even up to the grain boundaries. In contrast, however, they found that the high phosphorus specimens showed evidence of a two phase structure in both X-ray scans and metallography, and a definite interface could be distinguished between the ordered and disordered regions of the crystal, throughout the transformation. Additionally, they found that the domain size near grain and twin boundaries were smaller than within the grains. To explain these results they proposed a theory to describe the growth of colonies of domains, by the movement of an order–disorder interface, in the high phosphorus material, and the resultant increase in transformation rate.

Lehman and Kosel [7] concluded that an increase in phosphorus content increased the driving force for the LRO reaction in Ni_2Cr, resulting in an increase in the continuous ordering process and a decrease in the critical nucleus size for nucleation and growth which leads to a more rapid colony growth process. They cite, as supporting evidence for the above conclusion, the fact that, from X-ray diffraction measurements, the fractional lattice contraction upon ordering increased with phosphorus content, which suggests that phosphorus increases the driving force for the ordering reaction. Lehman and Kosel [7] report fractional lattice contractions of 0.43, 0.36 and 0.27% after ageing the solution annealed material for 10 h for the high phosphorus, 170 h for the medium phosphorus and 240 h for the low phosphorus materials, respectively. However, the present results indicate that 10, 240 and 288 h ageing at 500° C are required for complete order transformation for the high, medium and low phosphorus materials. Thus the fractional lattice contractions, measured by Lehman and Kosel [7], may be due to incomplete order transformation rather than to phosphorus content. This conclusion may be supported by the fact that, according to Lehman and Kosel's X-ray measurements, no effect of phosphorus on lattice constant of the disordered structure, in the solution annealed material was found.

4.2. Effect of cold rolling on the kinetics of order–disorder transformation in Ni_2Cr alloys with different phosphorus contents

It was found that cold rolling the low phosphorus material by 6% reduced the time for complete order transformation by 16% at 500° C ageing temperature, compared to the solution annealed material. However, increasing the amount of cold rolling to 12 and

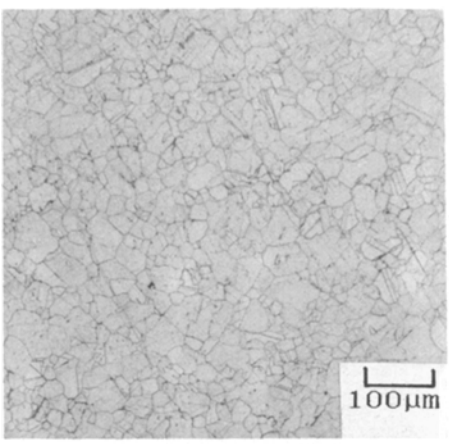

Figure 4 Microstructure of high phosphorus material solution annealed at 900° C, aged at 450° C for 10 h.

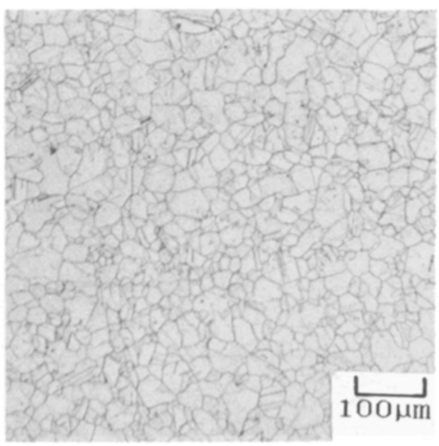

Figure 5 Microstructure of high phosphorus material solution annealed at 900° C, aged at 450° C for 120 h.

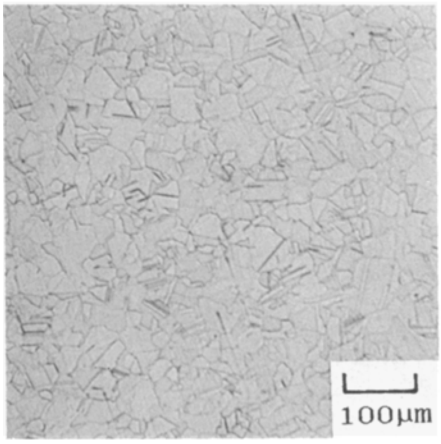

Figure 6 Microstructure of high phosphorus material solution annealed at 900° C, aged at 450° C for 288 h.

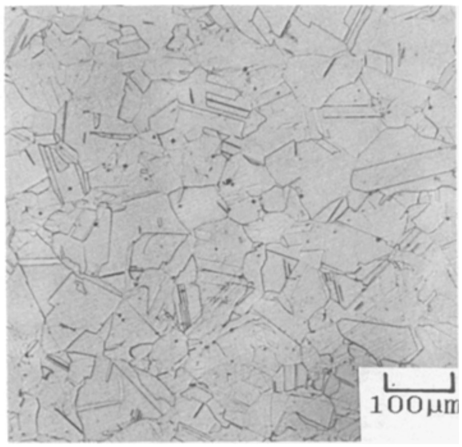

Figure 8 Microstructure of high phosphorus material solution annealed at 900° C, for aged at 500° C for 120 h.

21% produced no further changes in the time required for the transformation. On the other hand, ageing the low phosphorus material at 450° C followed by cold rolling reduced the time for complete ordering by greater than 22%.

The major effect of cold rolling is to increase the dislocation and point defect density in the crystal lattice. Since both types of defect can cause the spacing between atoms to be reduced due to compressional strains, the formation of the order transformation, which is accompanied by a lattice parameter decrease, is favoured. Thus cold rolling increases the driving force for nucleation and a higher transformation rate results.

For high phosphorus material, 6% cold rolling increased the time for complete ordering by more than 24 times, compared to the solution annealed material. In this case, the complete elimination of the effect of phosphorus on the rate of ordering, by cold rolling 6%, can only be explained by the trapping of phosphorus by dislocations and other defects introduced by the cold rolling. Increasing the amount of cold rolling to 12% increased the rate of order transformation by an additional 20%. This increase may be accounted for by the dislocation, point defect strain field effect, discussed previously. Increasing the amount of cold rolling to 21% produced no additional change in the rate of transformation, probably because the dislocation density had reached a saturation level. A similar explanation could account for the behaviour of the high phosphorus material aged at 450° C and cold rolled 21%. Although in this case the overall transformation rates are slower because the temperature is lower and the growth rates of the ordered domains are less.

For the medium phosphorus material aged at 500° C, 6% cold rolling had no effect on the rate of order transformation, compared to the solution annealed material. This may be accounted for on the basis of the previous arguments that cold rolling first eliminates the effect of phosphorus, which increases the time for complete ordering from 10 days to 12 days (equivalent to the low phosphorus in the solution annealed material) and secondly the introduction of dislocations and other defects decreases the time for complete ordering from 12 days for the low phosphorus solution annealed material to 10 days for the medium phosphorus material with 6% cold rolling. Thus the net effect of 6% cold rolling is to produce no change compared to that in the medium phosphorus solution annealed condition. Increasing the amount of cold rolling to 12% reduces the time for complete

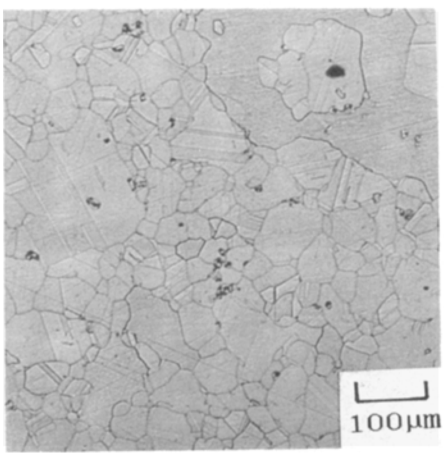

Figure 7 Microstructure of high phosphorus material solution annealed at 900° C, aged at 500° C for 10 h.

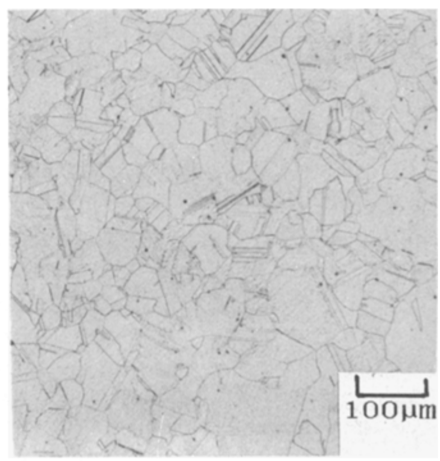

Figure 9 Microstructure of high phosphorus material solution annealed at 900° C, aged at 500° C for 288 h.

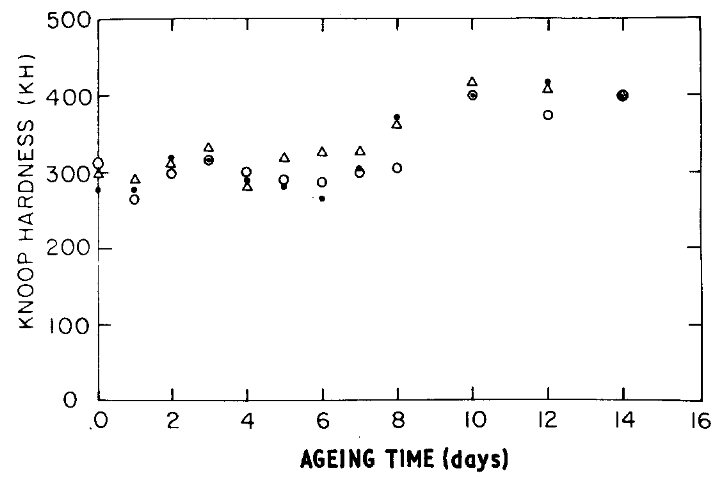

Figure 10 The progress of the order–disorder phase transformation measured by surface hardness increase. Cold rolled 6%, aged at 500° C. (△) 0.078 wt % phosphorus (●) 0.017 wt % phosphorus, (○) 0.002 wt % phosphorus.

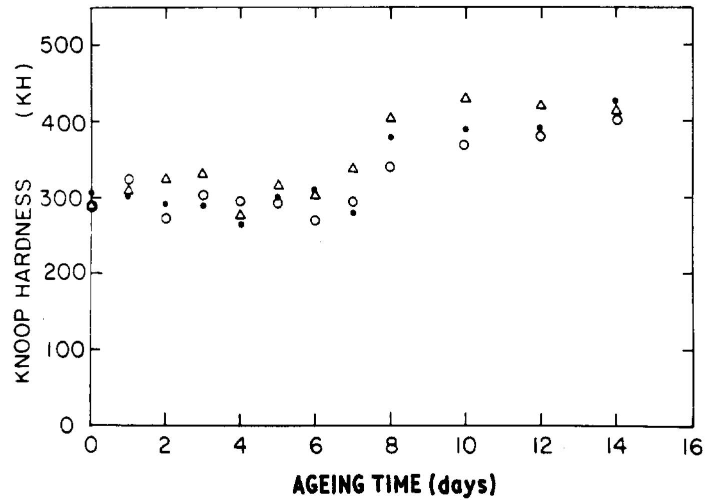

Figure 11 The progress of the order–disorder phase transformation measured by surface hardness increase. Cold rolled 12%, aged at 500° C. (△) 0.078 wt % phosphorus, (●) 0.017 wt % phosphorus, (○) 0.002 wt % phosphorus.

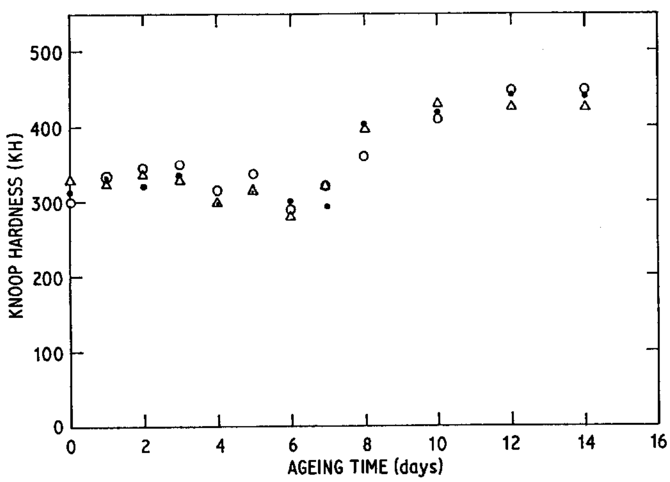

Figure 12 The progress of the order–disorder phase transformation measured by surface hardness. Cold rolled 21%, aged at 500° C. (△) 0.078 wt % phosphorus, (●) 0.017 wt % phosphorus, (○) 0.002 wt % phosphorus.

ordering because the dislocation density is increased further and the strain field enhances the nucleation of the ordered phase. As was argued for the high phosphorus, increasing the amount of cold rolling to 21% probably does not increase the total lattice strain significantly because the dislocation density is probably saturated. Similar effects to those described above were observed in the material aged at 450° C, although more time is required for the order transformation to reach completion, for reasons discussed previously.

5. Conclusions

It may be concluded, from the results presented here, that the rate of order transformation in Ni_2Cr alloys is significantly enhanced by increasing the phosphorus content. At the present time the atomic mechanism responsible for this enhancement is unclear.

Cold rolling increases the rate of transformation of low phosphorus material probably due to dislocation compressional strain fields.

Cold rolling completely eliminates the effect of phosphorus on the rate of order transformation, however, some enhancement of the rate of ordering is produced in this case due to the strain fields of dislocations and other lattice defects such as vacancies.

Decreasing the ageing temperature from 500 to 450° C produces a finer grain size, for the same ageing time, because the driving force for nucleation increased with decreasing temperature and the activation energy for growth was decreased.

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