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A study of the effects of phosphorus on the kinetics and mechanism of the order–disorder transformation in an Ni_2Cr alloy

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Three Ni_2Cr alloys, with phosphorus (P) contents of 0.002, 0.017 and 0.078 wt% were prepared as cast slabs, which were then thermomechanically treated to a final thickness of 0.38 mm, after which they were solution annealed at 900° C for 1 h and water quenched. The isothermal order–disorder transformations of the Ni_2Cr alloys were investigated in specimens aged at temperatures between 425 and 550° C, for times ranging from 2 h to 70 days, by surface hardness measurements and microstructural studies. From the surface hardness data, time–temperature–transformation (TTT) curves were constructed for each of the three alloys of different phosphorus content. It was found that increasing the amount of phosphorus greatly reduced the time required to start and complete the order transformation. However, it was found that the effect of phosphorus content on the rate of transformation was significantly reduced at ageing temperatures above 500° C. The results are discussed in terms of models for nucleation and growth of ordered phases.

1. Introduction

Nickel-based superalloys are designed for applications where high-temperature strength in corrosive environments is required. It has been found that the strength of these materials can be improved by thermal treatments which produce an ordered phase transformation. The Ni_2Cr alloy is used as a model system because a long-range order (LRO) transformation occurs, which is similar to that found in other nickel-based superalloys. On cooling below the critical temperature (T_c) of 572° C, a disordered face centred cubic structure transforms to a body centred orthorhombic superlattice by a continuous ordering process. The orthorhombic structure of the ordered phase has been confirmed by several workers using X-ray [1, 2], neutron [3, 4] and electron [5, 6] diffraction techniques. Previous studies have shown that the physical properties (corrosion resistance) and mechanical properties (tensile, surface hardness, creep strength, and hydrogen embrittlement) are greatly influenced by the degree of order–disorder transformation [7–12].

Many investigators have attempted to identify those factors which can influence the kinetics of the order–disorder transformation. There is some disagreement in the literature as to the exact value of the critical temperature (T_c) for the order–disorder transformation. Some investigators report T_c to be 590° C [3, 5], whereas others found T_c to be 572° C [13]. However, it is known that at a temperature of 500° C the order transformation proceeds at a fast rate [3].

The effect of phosphorus content and preliminary microstructure on the kinetics and mechanism of ordering in Ni_2Cr has been studied recently by Lehman and Kosel [14] and Abd-Elhady [15]. Lehman and Kosel studied the effects of pretreatments at 900 and 600° C on the kinetics of the order transformation in material aged at 500° C. In the high phosphorus material, he found that, for samples pretreated by annealing at 600° C, the time required for complete ordering was about three times that for the samples solution annealed at 900° C.

Abd-Elhady [15] investigated the effect of preliminary microstructure, established by thermomechanical processing, on the rate of ordering in Ni_2Cr alloys with three different phosphorus contents. Experiments were carried out on material solution annealed at 900° C, cold rolled 6, 12 and 21% and subsequently aged at 450 and 500° C. It was found that, for materials annealed at 900° C, increasing the phosphorus content caused a significant increase in the rate of ordering. However, for materials which were cold rolled prior to ageing, a decrease in the rate of ordering was observed for the high phosphorus material, whereas a slight increase in the rate of ordering was observed for the low phosphorus material.

Although several investigators have attempted to study the effect of phosphorus content and preliminary microstructures on the rate of ordering in Ni_2Cr alloys, the previous work is incomplete because insufficient data were collected to completely define the kinetics and mechanism of ordering. The current work was undertaken, therefore, to obtain a more detailed understanding of the kinetics of ordering in a model Ni_2Cr alloy by construction of isothermal

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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	0.014

transformation diagrams at low, medium and high phosphorus contents. Change in surface hardness and metallographic investigations were used to measure the degree of ordering and kinetics of the transformation.

2. Materials and experimental procedure

Three Ni_2Cr alloys, with phosphorus contents of 0.002, 0.017 and 0.078 wt %, were prepared as cast slabs by Cabot Corporation (Kokomo, Indiana, USA). The chemical composition of the three alloys is shown in Table I. The alloys were thermomechanically processed to obtain material of final thickness 0.38 mm, after which they were solution annealed at 900° C for 1 h followed by water quenching.

Samples from each alloy were aged at temperatures of 550, 520, 510, 505, 500, 475, 450 and 425° C (± 5° C), for times ranging from 2 h to 70 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 microhardness tester using a Knoop indenter with a 200 g load. The average of ten hardness measurements was taken for each of the heat-treatment conditions. The accuracy of the measurements was ± 10 KH.

3. Results

3.1. Surface hardness measurements

The surface hardness data, as a function of ageing time and temperature, were used to construct isothermal transformation diagrams for the three Ni_2Cr alloys with phosphorus contents of 0.002, 0.017 and 0.078 wt %. The surface hardness of the Ni_2Cr alloys with the three phosphorus levels, annealed at 900° C followed by water quenching, was found to be about 200 ± 10 KH, while for the ordered material the surface hardness was about 380 ± 10 KH.

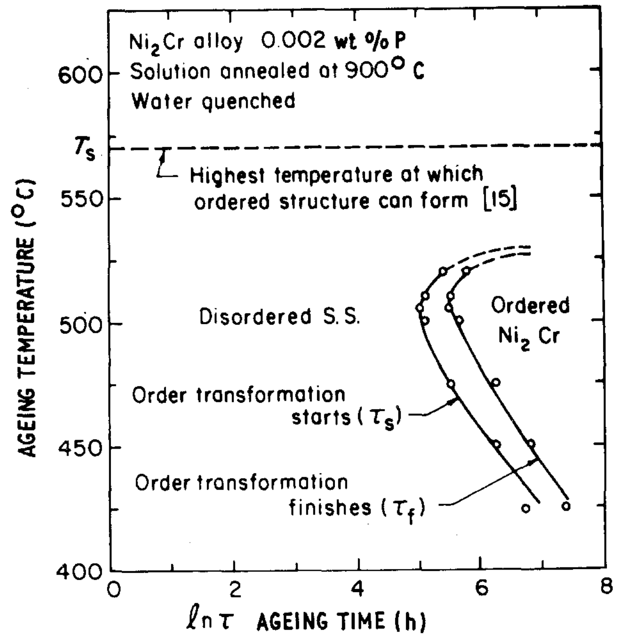

Figure 1 Isothermal transformation diagram for a Ni_2Cr alloy: 0.002 wt % P, solution annealed at 900° C for 1 h, water quenched.

The time required to start the order transformation (T_s) was defined as the time required to produce a change in surface hardness of 20% and after which the surface hardness continues increasing. The time required for complete order transformation (T_f) was defined as the time above which the change in surface hardness will be in the range of 5%.

Figs 1 to 3 show the isothermal transformation diagrams constructed from the surface hardness measurements, for the Ni_2Cr alloys with 0.002, 0.017 and 0.078 wt % phosphorus, respectively. From these figures it can be seen that, for the low and medium phosphorus materials, the maximum rate of order transformation (nose of the curve) occurs at 505 ± 5° C, whereas, for the high phosphorus containing material the maximum occurs at 500 ± 5° C. Therefore, increasing the phosphorus content from 0.002 to 0.078 wt % does not significantly change the temperature at which the rate of ordering is maximized. However, the same change in phosphorus content does greatly reduce the time required to start and complete the order transformation.

Fig. 4 shows a plot of the change in the logarithm of the time required for complete order transformation as a function of temperature for the three different phosphorus content alloys. Table II shows the time required to start and complete the order transformation, at ageing temperatures from 425 to 520° C, for the three phosphorus content alloys. From the data shown in Fig. 4 and Table II, it can be seen that the effect of phosphorus on the time for complete ordering depends greatly on the ageing temperature. At 500° C, increasing the phosphorus content from 0.002 to 0.078 wt % reduces the time required for complete ordering by about 96%. On increasing the ageing temperature to 505, 510 and 520° C, this

TABLE II Time required to start and complete order transformation for phosphorus content alloys

Ageing temp. (° C)	0.002 wt % P		0.017 wt % P		0.078 wt % P	
	t_s(h)	t_f(h)	t_s(h)	t_f(h)	t_s(h)	t_f(h)
520	216	312	192	264	48	192
510	168	240	96	192	24	96
505	144	240	96	171	10	48
500	168	288	120	240	2	10
475	240	504	180	336	3	24
450	480	912	240	504	4	48
425	812	1635	403	897	12	168

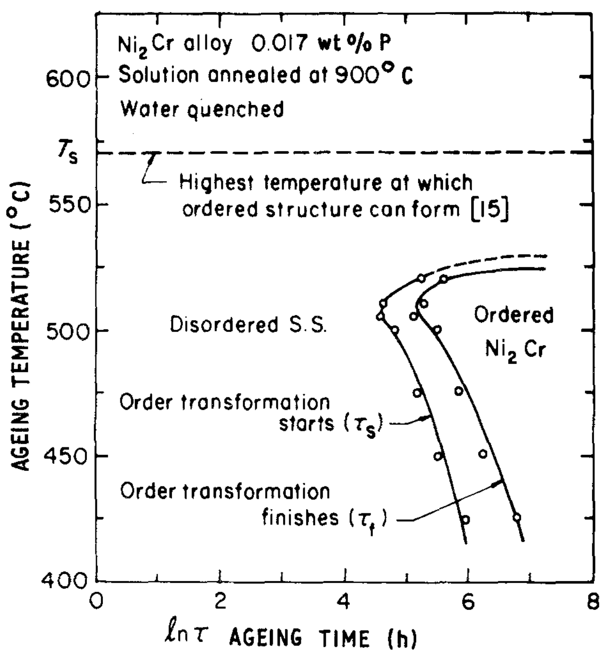

Figure 2 Isothermal transformation diagram for a Ni_2Cr alloy: 0.017 wt % P, solution annealed at 900° C for 1 h, water quenched.

percentage reduction in time decreases to about 80, 60 and 38%, respectively. However, at temperatures below about 500° C, there is no significant change in the percentage reduction of time required for complete ordering, due to change in phosphorus content, as the temperature is lowered to 425° C.

An activation energy of diffusion, Q, was calculated from the slopes of the curves shown in Fig. 4, using the data points for the three phosphorus contents obtained by ageing the materials at temperatures of 475, 450 and 425° C. For the low and medium phosphorus materials a value of Q in the range 22 to 24 kcal (~ 92 to 100×10^3 J) was obtained, whereas for the high phosphorus material, Q was found to be about 40 kcal ($\sim 167 \times 10^3$ J).

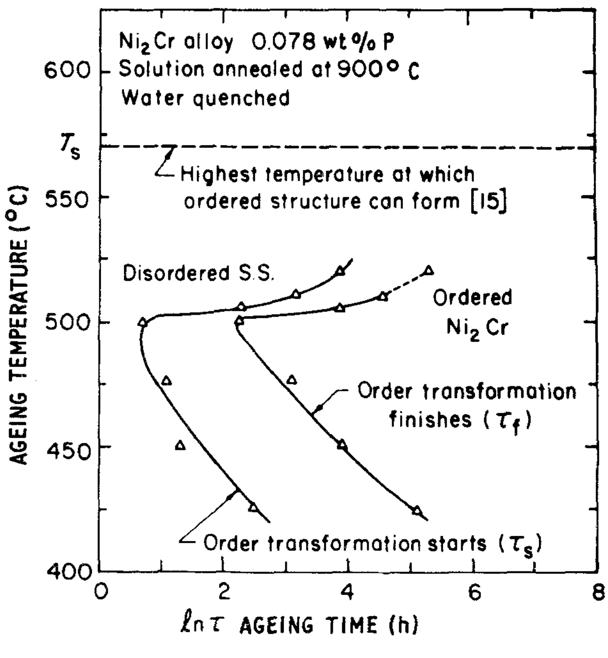

Figure 3 Isothermal transformation diagram for a Ni_2Cr alloy: 0.078 wt % P, solution annealed at 900° C for 1 h, water quenched.

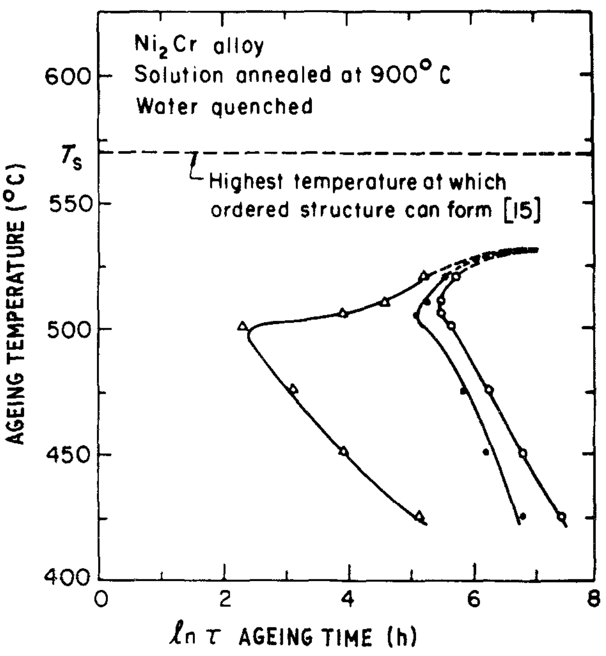

Figure 4 Effect of phosphorus content and ageing temperature on the time required for complete ordering in a Ni_2Cr alloy, solution annealed at 900° C for 1 h followed by water quenching. Phosphorus content: △, 0.078 wt %; ●, 0.017 wt %; ○, 0.002 wt %.

3.2. Metallographic study

For the metallographic studies the samples were prepared by grinding on SiC papers and finished by polishing on alumina and diamond wheels. The samples were then etched with a solution containing 75% hydrochloric acid with a few drops of hydrogen peroxide. It is of significance to note that, whereas the time required for revealing the microstructure in the high phosphorus material was only about 10 sec, more than 1 min was required for revealing the microstructure in the ordered low phosphorus material.

Figs 5 to 8 show the microstructures of the ordered Ni_2Cr material after ageing at temperatures of 450, 500, 505 and 520° C, for the time required for ordering to be completed (as shown in Table II). The grain sizes measured for the above microstructures were found to be 22, 65, 90 and 180 μm, respectively. Fig. 9 shows the microstructure of the ordered Ni_2Cr for the low phosphorus material after ageing at 500° C for 12 days. In this case the average grain size is about 90 μm.

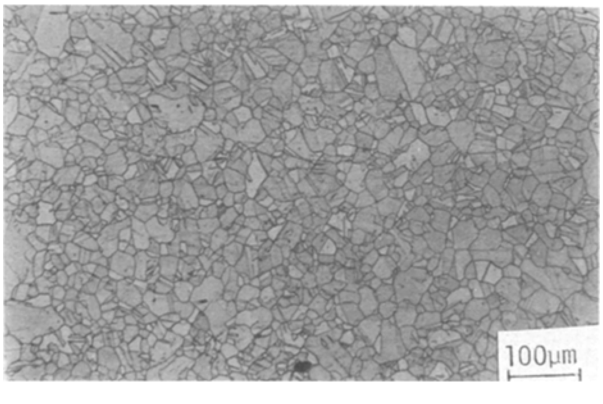

Figure 5 Microstructure of high phosphorus material solution annealed at 900° C for 1 h and water quenched, aged at 450° C for 48 h.

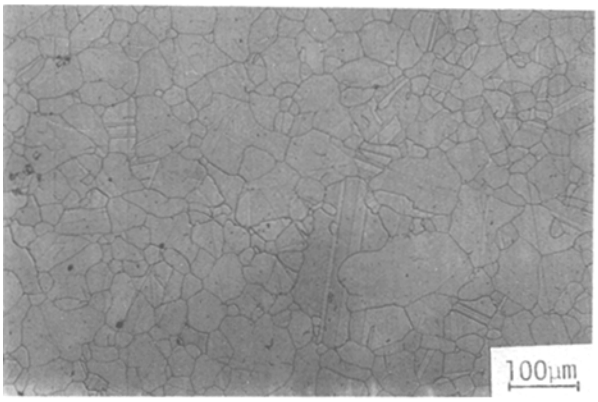

Figure 6 Microstructure of high phosphorus material solution annealed at 900° C for 1 h and water quenched, aged at 500° C for 10 h.

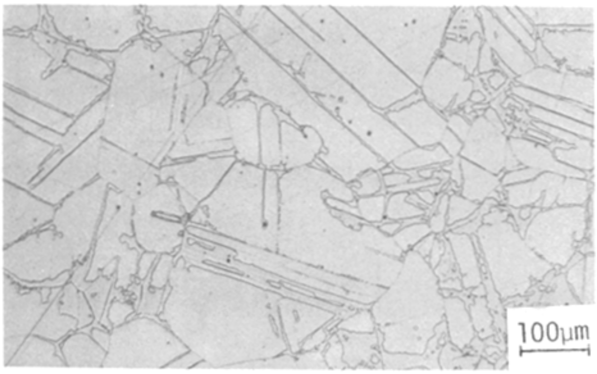

Figure 8 Microstructure of high phosphorus material solution annealed at 900° C for 1 h and water quenched, aged at 520° C for 192 h.

4. Discussion

The formation of a long-range superlattice from a disordered solid solution is now recognized as a first order transformation, which may occur by nucleation and growth processes. Provided that both the initial and final structures are single phases, ordering processes may involve atomic rearrangements without the need for long-range diffusion.

The nucleation rate for the order–disorder transformation can be increased considerably by increasing the degree of undercooling below T_c, which increases the driving force for the transformation. The growth rate, being controlled by an activation energy which is nearly temperature independent, decreases as temperature decreases. Thus nucleation and growth are the two independent parameters which control the rate of order transformation (as shown in Figs 1 to 3) and the grain size of the ordered structure (as shown in Figs 5 to 8).

Lattice parameter measurements have shown that a lattice contraction occurs during the order–disorder phase transformation and this is directly related to the phosphorus content of the alloy, i.e. a higher phosphorus content leads to a larger lattice contraction [14]. Since long-range ordering is accompanied by a lattice parameter decrease, and as phosphorus leads to a larger lattice contraction, increasing the phosphorus content should increase the rate of ordering by increasing the driving force for nucleation. On the other hand, from the activation energy measurements, it was found that increasing the phosphorus content from 0.002 to 0.078 wt % led to an increase in the activation energy for diffusion from 22 kcal ($\sim 92 \times 10^3$ J) to above 40 kcal, ($\sim 167 \times 10^3$ J) which indicates that increasing the phosphorus content greatly reduces the rate of diffusion.

The net effect of phosphorus on the rate of ordering can be seen from Figs 1 to 4, from which it can be seen that increasing the amount of phosphorus greatly reduces the time required to start and complete the order transformation. The effect of phosphorus can only be explained if the ordering process involves short-range atomic rearrangements, without the need for long-range diffusion. Therefore, it is the nucleation process, which greatly depends on the phosphorus content, which is the controlling factor for the rate of the order transformation.

At the ageing temperature of 500° C, the time required for starting and completing the ordering transformation is minimized for all three levels of phosphorus. This may be due to both nucleation and growth processes occurring at very fast rates. On increasing the amount of phosphorus, the time required to obtain a completely ordered structure was greatly reduced by 96%. This may be due to a higher rate of nucleation which is promoted by the higher phosphorus content (Figs 6 and 9).

At temperatures above 500° C, there is a reduction

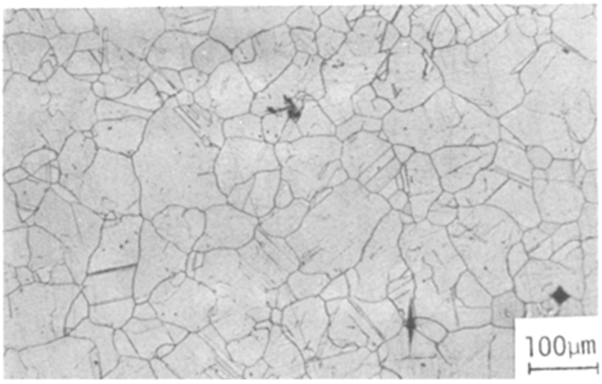

Figure 7 Microstructure of high phosphorus material solution annealed at 900° C for 1 h and water quenched, aged at 505° C for 48 h.

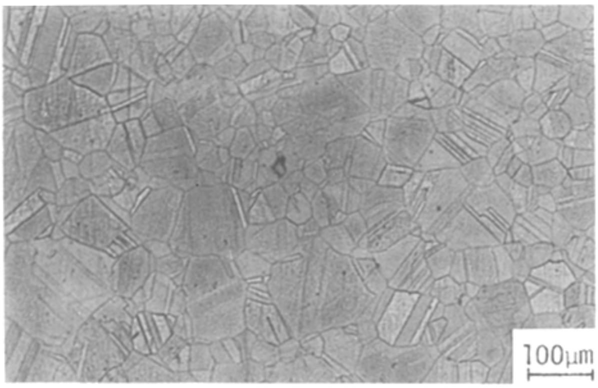

Figure 9 Microstructure of low phosphorus material solution annealed at 900° C for 1 h and water quenched, aged at 500° C for 288 h.

in the effect of phosphorus on the rate of ordering because as the ageing temperature approaches that of T_c there is a reduction in the rate of nucleation of the ordered phase, hence, more time is required to start and complete the transformation. Although the exact mechanism by which phosphorus affects the rate of nucleation is not fully understood, it appears to be related to the fact that the presence of phosphorus increases the lattice contraction which occurs during ordering. At temperatures above 500° C the atoms may have sufficient kinetic energy to overcome the effects of phosphorus on the atomic order.

At ageing temperatures below 500° C, decreasing the ageing temperature increases the time to start (t_s) and complete (t_f) ordering, without a significant change in the acceleration effect of phosphorus on the rate of the transformation. This result may be explained if one assumes that below 500° C there are two competing effects; the rate of nucleation and the rate of growth of the ordered domains. Decreasing the temperature below 500° C will increase the driving force for nucleation, due to undercooling; however, the rate of growth also decreases as the temperature decreases. The net effect of decreasing the ageing temperature below 500° C is that it takes longer times both to start and complete the ordering transformation for all three levels of phosphorus (Table II). On the other hand, there is no change in the effect of phosphorus, on the rate of order transformation, at temperatures below 500° C. This may be explained if decreasing the temperature has no effect on the lattice contraction which occurs during ordering due to the increased phosphorus content.

5. Conclusions

1. The rate of ordering in Ni_2Cr is maximized at an ageing temperature of 500 ± 5° C, for all three phosphorus levels. Increasing or decreasing the ageing temperature above or below 500° C reduces the rate of ordering, which means that the order transformation occurs by nucleation and growth process.

2. Phosphorus greatly increases the rate of ordering in Ni_2Cr during ageing in the temperature range 425 to 520° C.

3. The effect of phosphorus on the rate of ordering depends on the ageing temperature. At 500° C, the increase in the rate of ordering due to phosphorus is maximized. Increasing the ageing temperature above 500° C decreases the effect of phosphorus, which is minimized at 520° C. At ageing temperatures below 500° C there is no change in the effect of phosphorus on the rate of ordering.

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