A study of the effects of phosphorus on the kinetics of recrystallization and mechanical properties of Ni_2Cr alloy

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The recrystallization process of 50% cold-rolled Ni_2Cr alloy, with phosphorus (P) contents of 0.002, 0.0017 and 0.078 wt% was investigated, in specimens annealed at temperatures from 600 to 100° C, for times ranging from 10 to 60 min, as functions of surface hardness and microstructure change. It was found that annealing at temperatures below 700° C for times less than 30 min resulted in an increase in hardness from about 430 to 50 KH, depending on the phosphorus content. This increase was thought to be due to interactions between dislocations and the strain fields of impurity atoms such as phosphorus. It was also found that phosphorus increases the activation energy of the recovery and recrystallization process, from about 23 to 27 kcal mol^{-1} for low and medium phosphorus material to 43 kcal mol^{-1} for high phosphorus material. The effects of thermomechanical treatment and order transformation on the mechanical properties of Ni_2Cr alloy with 0.002 and 0.078 wt% P were also studied. It was found that 50% cold-working increases the yield stress of 0.002 and 0.078 wt% P materials by 190% and 145%, respectively, compared to the solution-annealed materials. Similarly, an increase in yield stress of 106% and 85%, respectively, was observed for 0.002 and 0.078 wt% material, which was transformed to the long-range ordered condition.

1. Introduction

The nickel chrome supperalloys 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 (P) and sulphur (S) to grain boundaries.

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 transformation (LRO). It has been reported by several authors [1–4], that on cooling below a critical temperature, T_c, of about 570° C, Ni_2Cr transforms from a disordered face-centred cubic structure to a body centred orthorhomic superlattice.

The strength, plastic properties and corrosion resistance of the nickel-based superalloys have been investigated by many workers. Warlimont [5] found that 50% cold-working followed by annealing below the recrystallization temperature increases the proof stress at small bending strains by 36 to 97%. The magnitude of the increase is related to the atomic misfit of the solute. The hardening effect was attributed to segregation of solute atoms to dislocations.

Lai and Thompson [6] investigated the effect of thermal ageing on the mechanical properties of Ni–Cr–Mo–Fe alloys and Svistunova [7] studied the structure and mechanical properties of Ni–Mo alloys produced by annealing at temperatures between 500 and 900° C.

Abd-Elhady and Sargent [8], investigated the effects of cold-rolling and phosphorus content on the kinetics of long-range order transformation in Ni_2Cr. Further studies by Abd-Elhady and Sargent [9], on the same material, were undertaken to construct the isothermal time–temperature transformation diagram for three levels of phosphorus content.

The purpose of the present work was to study the kinetics of recovery and recrystallization processes of 50% cold-worked Ni_2Cr alloy with three levels of phosphorus. Also investigated were the different mechanisms of strengthening observed in low phosphorus, compared to high phosphorus materials.

2. Materials 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). The chemical compositions of the alloys are given in Table I. The three alloys were thermomechanically processed to obtain material of final thickness 3.3 mm with 50% cold-work.

Tensile specimens and specimens for surface hardness measurements and microstructural investigation

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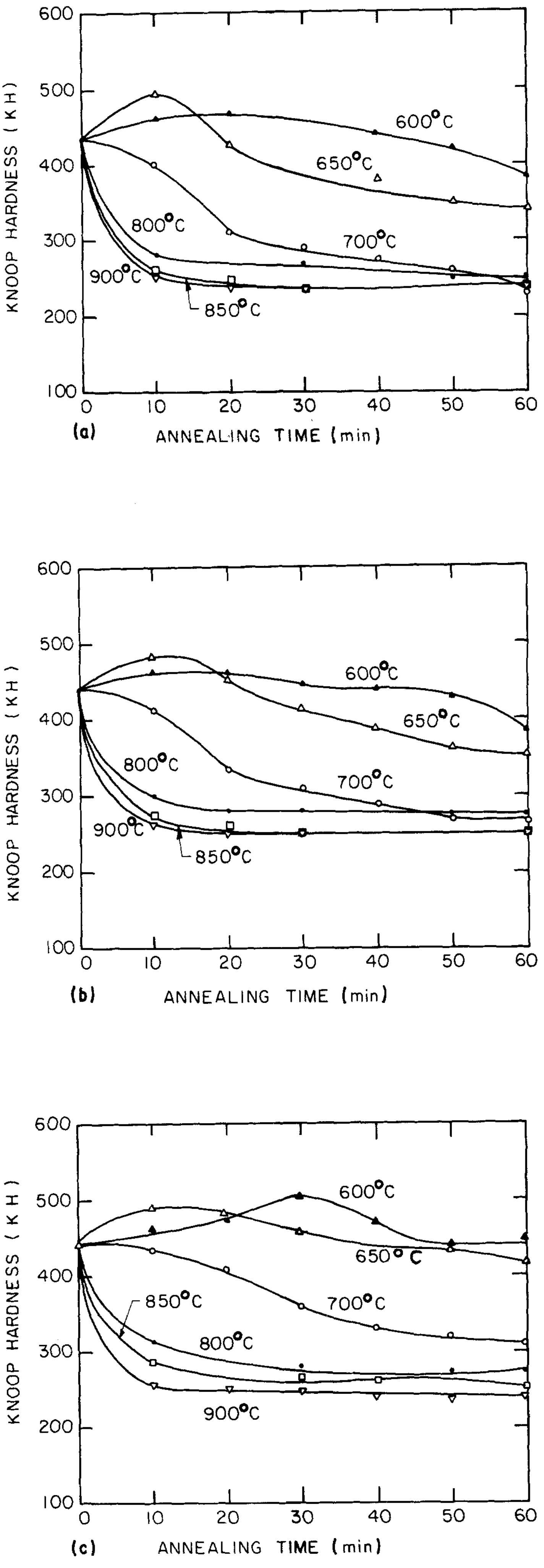

Figure 1 Charge in surface hardness of 50% cold-worked Ni_2Cr as a function of annealing time and temperature. (a) Low phosphorus material (0.002 wt % P); (b) medium phosphorus material (0.017 wt % P); (c) high phosphorus material (0.078 wt % P).

TABLE I Chemical composition 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

were prepared from each alloy. The samples were heat treated by two different schedules:

(A) annealing at temperatures of 600, 650, 700, 800, 850, and 900° C for times of 10, 20, 30, 40, 50, and 60 min at each of the above temperatures;

(B) the low phosphorus (0.002 wt %) and high phosphorus (0.078 wt %) materials were aged for 14 days at a temperature of 500° C after one of the following pretreatments (i) 50% cold-work, (ii) 50% cold-work followed by solution annealing at 900° C for 2 h, followed by water quenching.

Surface hardness measurements were carried out on a LECO M-400 microhardness tester with a 200 g load. An average of ten hardness measurements were taken for each heat-treatment condition. The accuracy of the measurements was ± 10 KH.

The tensile tests were carried out on a Rihel Testing machine. The average of three tests was taken for each heat-treatment condition. The accuracy of each measurement was ± 50 MPa. Microstructural investigations were carried out on a Neophot 21 microscope.

3. Results and discussion

3.1. Effects of phosphorus content on the kinetics of recrystallization of 50% cold-worked material

The change in surface hardness as a function of annealing time and temperature, for low, medium and high phosphorus materials, is shown in Figs 1a, b, and c, respectively. The annealing behaviour is significantly different at temperatures above and below 700° C. At temperatures of 600 and 650° C, there is a slight increase in surface hardness with increased annealing temperature for all three phosphorus levels. The increased hardness may be caused by the movement of impurities such as phosphorus, sulphur, silicon or carbon to the strain fields of dislocations, which are thus immobilized. Comparing Figs 2a, and b, shows that no significant change in microstructure occurs when the low phosphorus material in the initially 50% cold-rolled condition is annealed at a temperature of 600° C for 30 min. Increasing the annealing time to 60 min reduces the surface hardness slightly, probably due to the

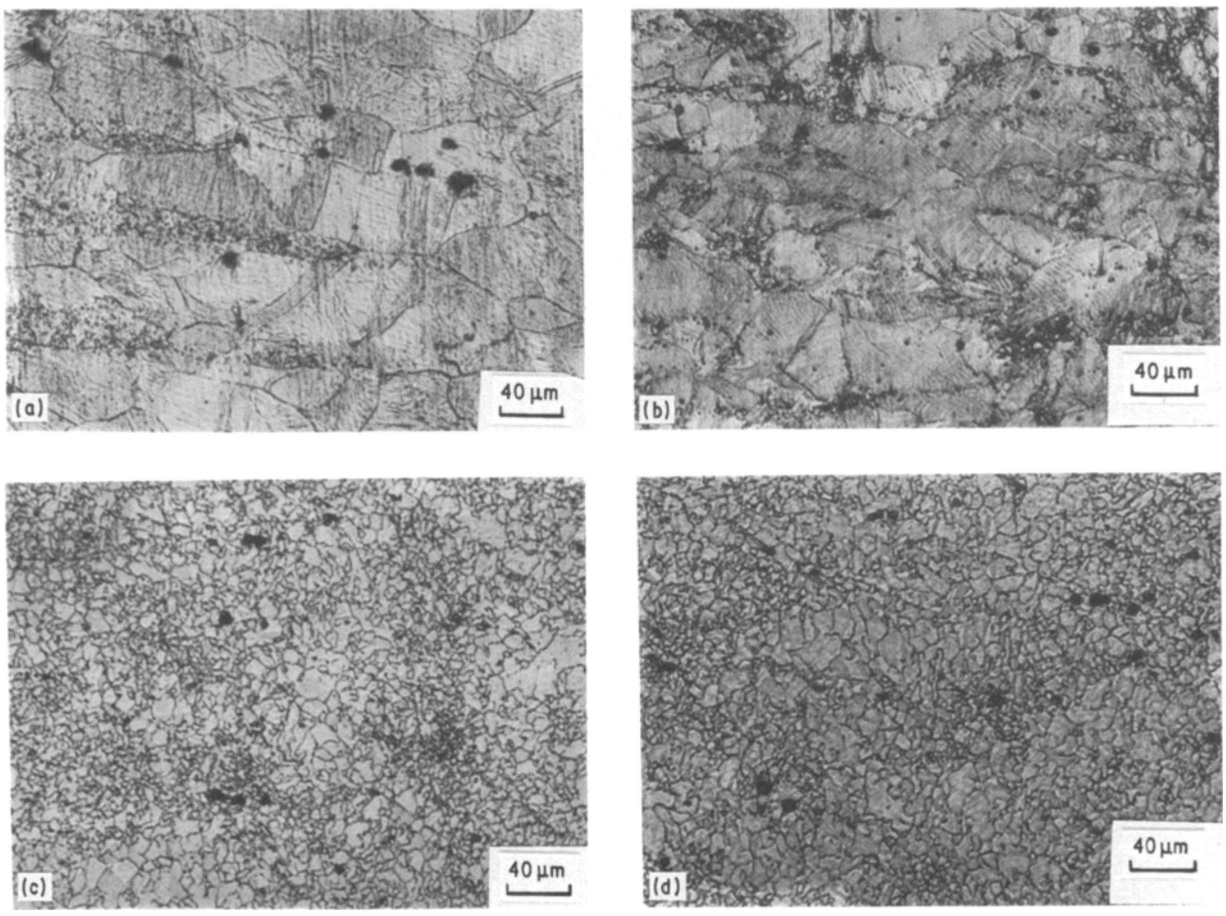

Figure 2 The microstructure of low phosphorus material (0.002 wt % P). (a) As cold-rolled, (b) annealed at 600° C for 30 min, (c) annealed at 700° C for 30 min, (d) annealed at 800° C for 30 min.

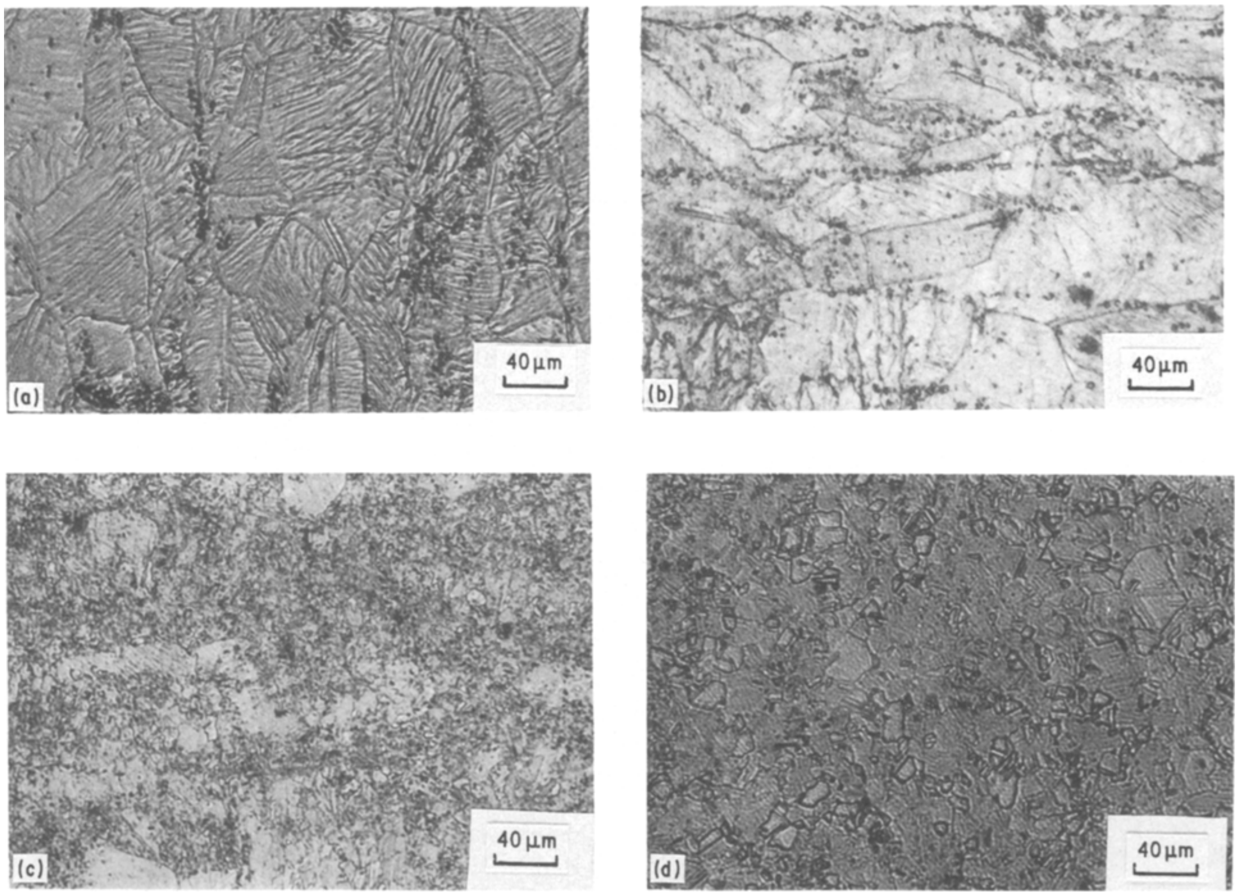

Figure 3 Microstructures of high phosphorus material (0.078 wt % P). (a) As cold-rolled, (b) annealed at 600° C for 30 min, (c) annealed at 700° C for 30 min, (d) annealed at 900° C for 30 min.

stress relief produced by slight dislocation rearrangements.

Increasing the annealing temperature to 700° C, produces a sharp decrease in surface hardness for all three phosphorus content materials, probably due to recrystallization. An activation energy for the recrystallization process was computed from the rate of decrease of the surface hardness with increased annealing temperature for temperatures above 650° C. It was found that increasing the phosphorus content increases the activation energy for the recrystallization process from 23 to 27 kcal for the low and medium phosphorus material to about 43 kcal for the high phosphorus material. These values agree with those reported previously [9], where it was concluded that the effect of increasing the phosphorus content from low to high was to greatly reduce the diffusion rate of phosphorus through the matrix.

It can be seen from Fig. 2c, that the microstructure of the low phosphorus material annealed at 700° C for 30 min is considerably refined, when compared to that of the cold-rolled material in Fig. 2a, because of recrystallization. At times loger than 30 min, no further changes in surface hardness are measured, which indicates that the microstructure is fully recovered by the recrystallization process. Fig. 2d, shows the microstructure of the fully recrystallized material, after annealing the low phosphorus material at 800° C for 30 min. Similar microstructural changes were observed when the high phosphorus material was annealed, as can be see from Figs 3a to d.

3.2. Effect of phosphorus content, annealing time and temperature on the tensile mechanical properties of the 50% cold-worked material

The change in tensile properties; ultimate tensile strength (UTS), yield stress (YS), percentage elongation to fracture (A%), and percentage reduction in area (Z%), for the low and high phosphorus materials, after annealing at temperatures between room temperature and 1000° C for 30 min, are shown in Figs 4a and b, respectively. In both low and high phosphorus materials the yield stresses and tensile strengths were found to decrease significantly when annealed at temperatures above about 650° C. At about the same annealing temperature both the percentage elongation to fracture and the percentage reduction in area show large increases. These changes in properties are clearly related to the onset of recrystallization at this annealing temperature, in agreement with the surface hardness data and the microstructural observations. In the high phosphorus material the percentage reduction in area shows a slight drop initially, at annealing temperatures between room temperature and about 600° C. This may be related to the precipitation of phosphorus and other impurities to dislocations as discussed previously.

3.3. Effects of phosphorus content and the order–disorder transformation on the mechanical properties of Ni_2Cr alloy

The effect of the order–disorder transformation on the

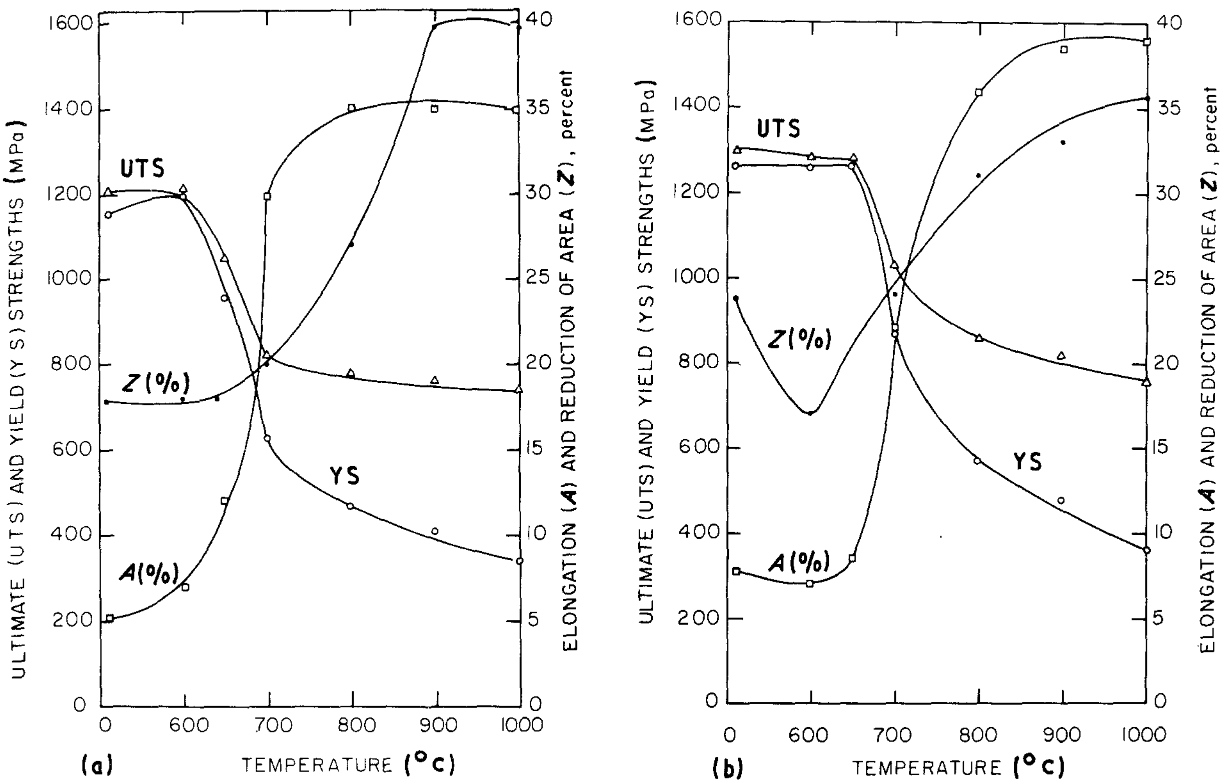

Figure 4 Charge in tensile properties of 50% cold-rolled Ni_2Cr after annealing at different temperatures (a) for low phosphorus material (0.002 wt % P), (b) for high phosphorus material (0.078 wt % P).

tensile properties of Ni_2Cr are shown in Figs 5A and B, for the low and high phosphorus materials, respectively. Table II summarizes the mechanical property data obtained for the four thermomechanical test conditions for the two phosphorus contents. From Figs 5A and B, and Table II, it can be seen that the effect of phosphorus on the tensile properties, under these thermomechanical treatment conditions, is negligible, with the exception that increasing the phosphorus content significantly affects the percentage reduction in area (Z%). In the material solution annealed at 900° C for 2 h, followed by water quenching and that similarly treated but aged at 500° C for 14 days, a decrease in the percentage reduction in area was observed. Whereas, in the material which was 50% cold-rolled or 50% cold-rolled followed by ageing at 500° C for 14 days, there was an increase in the percentage reduction in area, with increased phosphorus content.

In the solution-annealed condition, the structure of the material is disordered α. In tension the material fails by ductile rupture [10]. Ageing the above heat-treated material at 500° C for 14 days causes the long-range order transformation to occur in which the disordered f c c solid solution is transformed to a body centred orthorhombic superlattice Ni_2Cr. In this case the material failed in tension by a brittle mode due to cleavage separation of the domain boundaries. This type of failure is probably due to the segregation of impurities such as phosphorus, sulphur, silicon and carbon to boundaries of the ordered domains. The reduced ductility is also accompanied by an increse in the strength properties, although again there is no significant difference observed in the yield of ultimate strength properties when the phosphorus content is increased from low to high.

Cold-working the solution-annealed material by

TABLE II

Material condition	Surface hardness (KH)		Ultimate tensile strength, UTS (MPa)		Yield strength, YS (MPa)		Elongation, A (%)		Reduction in area, Z (%)	
	0.002 WT % P	0.078 WT % P	0.002 WT % P	0.078 WT % P	0.002 WT % P	0.078 WT % P	0.002 WT % P	0.078 WT % P	0.002 WT % P	0.078 WT % P
(a) Solution annealed at 900° C for 2 h followed by water quenching	240	240	760	832	397	448	32	33	40	33
(b) Solution annealed at 900° C for 2 h followed by water quenching and aged at 500° C for 14 days	445	434	1200	1216	819	832	12	12	10	11
(c) 50% cold-worked	430	440	1200	1280	1152	1100	4	6	18	24
(d) 50% cold-rolled followed by ageing at 500° C for for 14 days	620	500	1440	1344	1216	1250	7	4	3	7

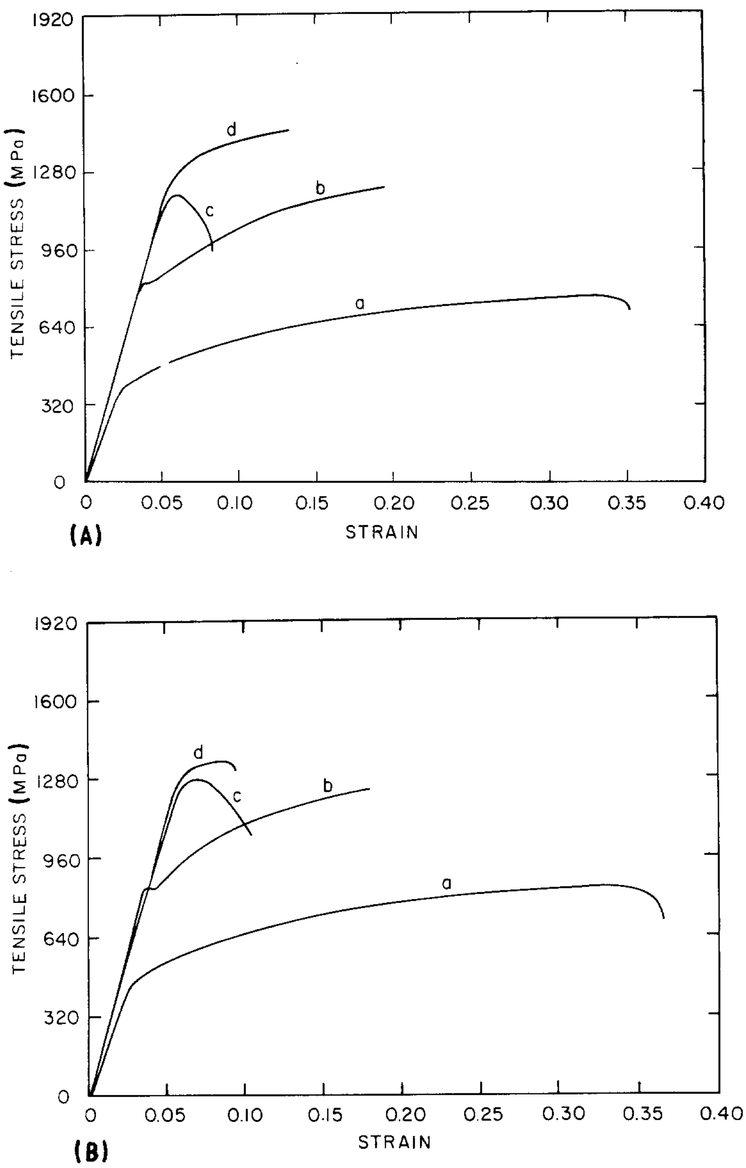

Figure 5 Effect of cold-rolling and order–disorder transformation on the tensile properties of Ni_2Cr alloy. (A) Low phosphorus material (0.002 wt % P), (B) high phosphorus material (0.07 wt % P). Curves (a) to (d) refer to the material condition as given in Table II.

50% significantly increased the yield and flow stresses and reduced the ductility compared to the solution-annealed condition. Increasing the phosphorus content in this condition caused the percentage elongation to fracture to increase by about 30%, but did not change the other tensile properties. The type of fracture observed was ductile rupture with little prior necking of the specimen. Ageing the 50% cold-rolled material at 500° C for 14 days to produce the ordered structure resulted in both increased strength and ductility. These differences in mechanical properties between the ordered structure and the cold-rolled structure may be due to the different interactions between dislocations, superdislocations and solute atoms. The type of failure in the long-range ordered 50% cold-rolled material was found to be cleavage separation along ordered domain boundaries.

4. Conclusions

1. Annealing the cold-rolled low, medium and high phosphorus content Ni_2Cr, at temperatures below the recrystallization temperature (600 and 650° C), for short times (from 10 to 30 min), hardens the material.

2. At annealing temperatures above the recrystallization temperature (above about 650° C), phosphorus increases the activation energy of recovery and recrystallization, from 23 to 27 kcal, for low and medium phosphorus material, to about 43 kcal for high phosphorus material.

3. Thermomechanical processing (cold-rolling and heat treatment to bring about the order transformation), can be used to control the mechanical properties of Ni_2Cr alloy.

4. Ordering of the cold-rolled material significantly increases its brittleness.

5. Other than the percentage reduction in area, phosphorus was found to have no appreciable effect on the mechanical properties of Ni_2Cr.

Acknowledgements

The authors wish to thank AMIDEAST, Mission Department Ministry of Higher Education, Cairo, Egypt and the Egyptian Cultural and Educational Bureau, Washington DC, for providing financial support to Dr Mohamad Abd-Elhady. The authors are also grateful to Cabot Corporation, Wrought Products Division, Technology Department for providing the materials and technical assistance. The authors also thank Dr A. E. El-Nikhaily for his thoughtful suggestions.

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Received 24 January
and accepted 14 March 1986