

Kinetics of ordering in NiPt

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The kinetics of ordering for an almost equiatomic NiPt alloy were measured by X-ray diffraction. The measurements were carried out at the temperature of annealing between 390 and 570°C.

The results show that the transition from a disordered to an ordered state can be attributed to two processes: one is a nucleation of ordered zones and their growth and the other is a homogeneous ordering process. The latter is dominant at low temperatures (< 500°C) and nucleation-and-growth kinetics are dominant at higher temperatures.

1. Introduction

Below the critical temperature the equiatomic NiPt alloy orders [1] in the same way as CuAu and consequently the kinetics of ordering of both systems are supposed to be similar. The most revealing work in this field was published by Borelius [2], Dienes [3] and Kuczynski *et al* [4] on CuAu. Jones and Sykes [5] studied Cu₃Au and Newkirk *et al* [6] studied CoPt alloys. This last system was recently also investigated by Southworth [7] using the field-ion microscope.

Three types of ordering kinetics can account [8] for most of their results: (a) homogeneous ordering; (b) nucleation and growth of ordered domains; and (c) the creation of antiphase domains all over the crystal and the growth of some of them by absorbing the others.

Dienes [9] derived the equations for process (a) using simple chemical rate theory. Borelius [2] and Newkirk *et al* [6] divided the process into two ranges: a range where there is a *continuous* shift of X-ray diffraction lines towards positions characteristic of the ordered state and a range where one can see both the ordered and the disordered phases while one is growing and the other is disappearing. Borelius (CuAu) found homogeneous ordering at lower temperatures and the nucleation and growth at the high temperatures, while Newkirk *et al* (CoPt) found the opposite. Jones and Sykes [5] decided that antiphase domain coalescence (process c) is the one that is occurring.

Most of these studies were carried out with the help of resistivity measurements, while some measured changes in hardness and some also involved X-ray diffraction measurements. The diffraction measurements, however, were used mostly to obtain a qualitative information about the mechanism of ordering, while quantitative information was obtained from resistivity measurements on quenched samples. The present work is a direct X-ray diffraction analysis and all the measurements were made at the actual temperatures, i.e. the order parameter was measured from the intensity of the superlattice lines at the tempering temperatures.

2. Experimental procedure

The alloy was prepared from high purity nickel and platinum (better than 99.9%) pure by Engelhardt Industries in button form. The composition, as checked subsequently by chemical analysis, was 48.4 at. % Ni and the rest Pt. Fine powder was obtained by filing the button and sieving the powder through a 300 mesh per inch sieve. Powder briquettes 25 × 12 × 1 mm were obtained by pressing the powder at a pressure of 5000 psi at room-temperature. The briquettes were then sintered at 900°C for a few hours in a furnace with a reducing atmosphere.

The sample obtained in this way was used to measure X-ray diffraction patterns with a Picker X-ray goniometer. A Philips tube [10] was the source of the CoK_α radiation. The diffracted

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beam was monochromated with a LiF monochromator and measured by a proportional counter with a single channel analyser.

To make measurements at high temperatures a small diffractometer furnace was built. Special care was taken to ensure that there were no gradients of temperatures ($\pm 1^\circ\text{C}$) across the specimen. During the heating the specimen was bathed in a flowing atmosphere of Ne(14% H). The furnace had an outer shield with a mylar window through which the X-rays entered the furnace and left it after diffraction.

To measure the kinetics of ordering, the sample was first ordered at 500°C for 24 to 30 h and then disordered at 750°C . It was then quickly cooled to the annealing temperature and held at this temperature for the duration of the measurement. A diffraction run was made at this temperature every 20 to 30 h and the order parameter S calculated. When S reached a value of about 0.9 the sample was again disordered at 750°C and cooled quickly to a new measuring temperature. The temperature was kept constant within $\pm 3^\circ\text{C}$ during the run. The intensity of the diffraction lines was measured within an accuracy of 2% and using step scanning in 2θ .

3. Results

Kinetics measurements were done in the range of temperatures from 390 to 570°C at intervals of 30°C . The results could be divided into three different ranges: a low-temperature region (390 to 420°C), an intermediate-temperature region (450 to 540°C) and a high-temperature region ($\geq 570^\circ\text{C}$). The (200) peak decomposes into the two separate (200), (002) peaks during ordering (Figs. 1, 2 and 3). At low temperatures, e.g. at 390°C as exemplified in Fig. 1, we can see the co-existence of the disordered (200) peak with the ordered (002), (200) peaks. It can also be seen clearly that while the ordered peaks are growing their separation is growing also. At intermediate temperatures (e.g. 480°C , Fig. 2) the changes in order are much quicker and the disordered peak disappears after 18 h of annealing, but one can still see the continuous shifting of the ordered peaks. At high temperatures, e.g. 570°C , the ordered peaks grow at the expense of the disordered peak but they do not shift considerably. The reaction in this region is very slow and the disordered peak is still visible even after more than 200 h of annealing.

Figs. 4, 5 and 6 show the changes in the (110) superlattice line. It is clearly seen that while the

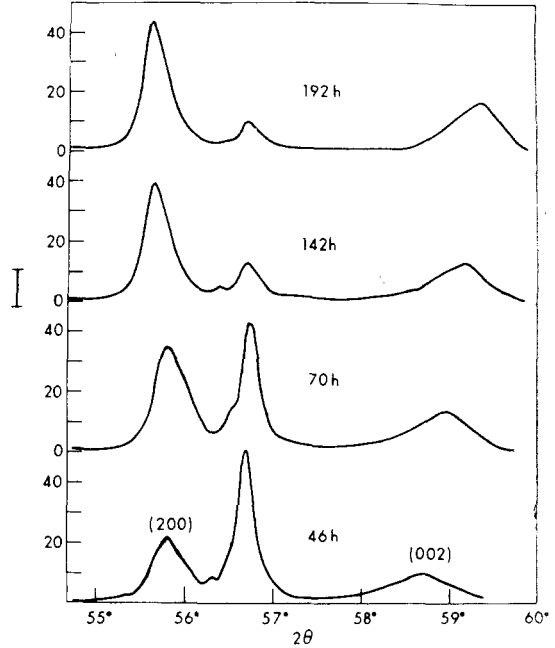


Figure 1 The decomposition of the (200) fundamental line into (200) and (002) superlattice lines during ordering by isothermal annealing at 390°C .

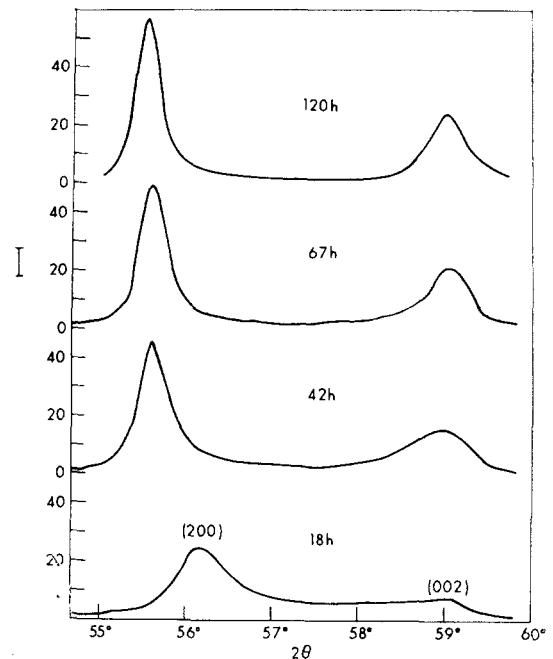


Figure 2 The decomposition of the (200) fundamental line during ordering by isothermal annealing at 480°C .

lines from the 390 and 480°C runs show growth of the mean ordered domain size, the line from the 570°C run show a nearly constant breadth

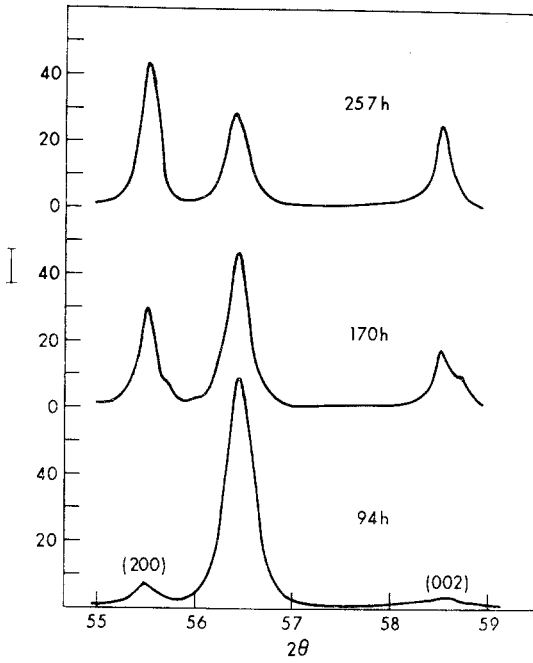


Figure 3 The decomposition of the (200) fundamental line during ordering by isothermal annealing at 570°C.

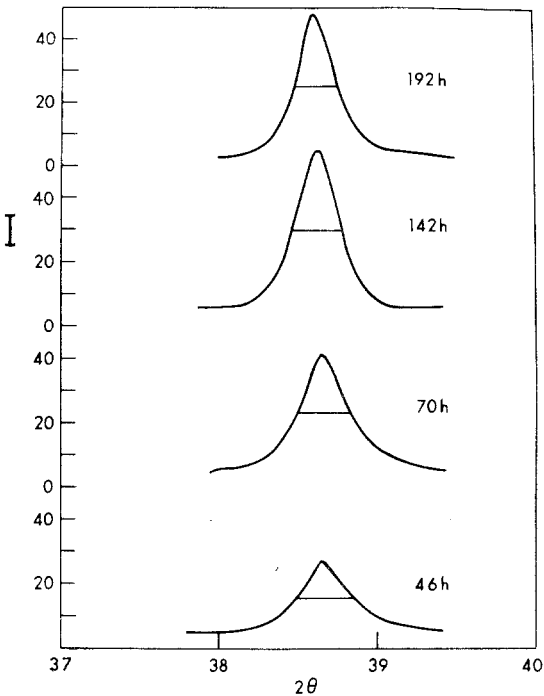


Figure 4 Changes in the (110) superlattice line during ordering by isothermal annealing at 390°C.

for all values of S . The integrated intensity of the superlattice line increases with time in all cases.

The critical temperature is approximately 870 K. At this temperature we begin to see ordered and disordered domains together. The

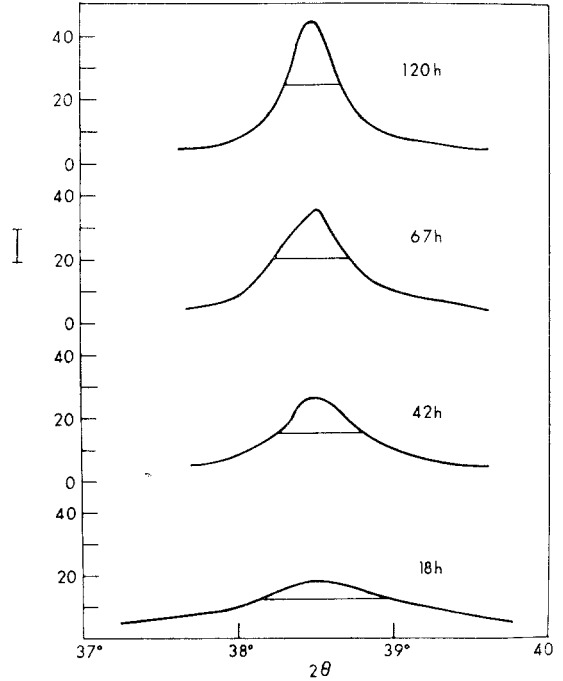


Figure 5 Changes in the (110) superlattice line during ordering by isothermal annealing at 480°C.

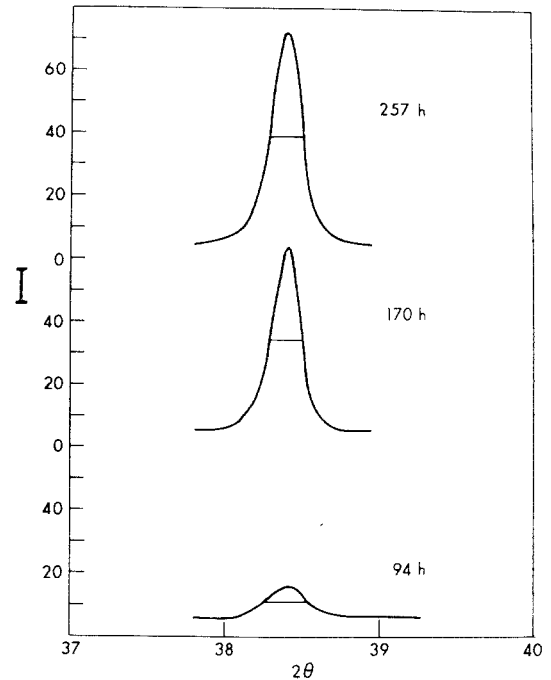


Figure 6 Changes in the (110) superlattice line during ordering by isothermal annealing at 570°C.

equilibrium value of S is not less than 0.98 at all the temperatures at which kinetics measurements were made.

Fig. 7 gives a plot of $\ln t_{1/2}$ versus $1/T$, where $t_{1/2}$ is the time to achieve $S = 1/2$. This plot is linear and gives an activation energy of $Q/R = 11000$ K or 21.9 kcal/mol.

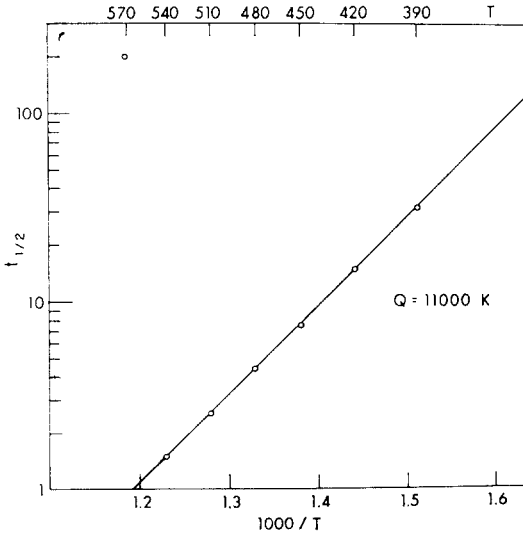


Figure 7 The temperature dependence of the relaxation time $t_{1/2}$ (the time to achieve an order parameter of $S = 0.5$).

4. Discussion

As stated in the introduction the most important problem here is to find out whether the kinetics of ordering in NiPt can be associated with one of the following reactions: (a) homogeneous ordering; (v) ordered domain growth; and (c) anti-phase domain coalescence.

First let us check hypothesis c. This is not really an ordering process because usually in this stage the domains are large enough to make the fraction of atoms in disordered state very small and essentially the "ordering" proceeds at constant S . Consequently, one should find no alteration in the fundamental lines and only a sharpening of the superlattice lines at constant integrated intensity. This is not the case here and so this hypothesis cannot hold.

Homogeneous ordering (hypothesis a) will give rise to a gradual shifting of the fundamental lines because usually the lattice parameter will be a function of the degree of long-range order.

Similarly, the superlattice lines will shift during ordering. These characteristics are seen in NiPt for the annealing temperatures of 390 and 480°C but not for the specimen annealed at 570°C. It seems then that at the low temperatures of ordering we have homogeneous ordering and at the highest temperature of ordering an ordered domain growth may be the prevalent mechanism.

To check this point further, let us try to evaluate the ordering rates under the assumption that the ordering is homogeneous.

From simple kinetics of phase-transformations [11] we can write for the rate of ordering in NiPt:

$$\frac{dS}{dT} = Ae^{-Q/RT} \left[1 - \exp\left(\frac{\partial F(S)}{\partial S} \cdot \frac{4}{RT}\right) \right] \quad (1)$$

where Q is the activation energy and F is the free energy for ordering.

In the Bragg-Williams approximation [12] the order-dependent part of the free energy per mole can be written as

$$\frac{F(S) - F(0)}{R} = \frac{\Delta F(S)}{R} = U(S) + \frac{T}{2} [(1 + S) \ln(1 + S) + (1 - S) \ln(1 - S)] \quad (2)$$

Here $U(S) = -U_0 S^2$ (Bragg-Williams approximation). If this is substituted in Equation 2, then a differentiation of the latter can be used with Equation 1 to yield

$$\frac{dS}{dT} = Ae^{-Q/RT} \left[1 - \exp\left(8U_0 S/T\right) \left(\frac{1 + S}{1 - S}\right)^2 \right] \dots (3)$$

This is equivalent to the Dienes equation [9] obtained from the chemical rate theory with $A = K(1 - S)^2$, K being the rate constant and

$$\frac{V}{8R} = U_0.$$

The Bragg-Williams free energy (Equation 2) gives the well-known S versus T curve and will not fit a first order transition where S drops sharply from a value near $S = 1$ to $S = 0$ at T_c , as is the case in NiPt.

For this reason we take:

$$U(S) = \frac{-T_c}{2} [(1 + S) \ln(1 + S) + (1 - S) \ln(1 - S)]$$

so that Equation 2 can now be written as

$$\frac{F(S) - F(0)}{R} = \frac{\Delta F(S)}{R} = \frac{-(T_c - T)}{2} [(1 + S) \ln(1 + S) + (1 - S) \ln(1 - S)] \quad (4)$$

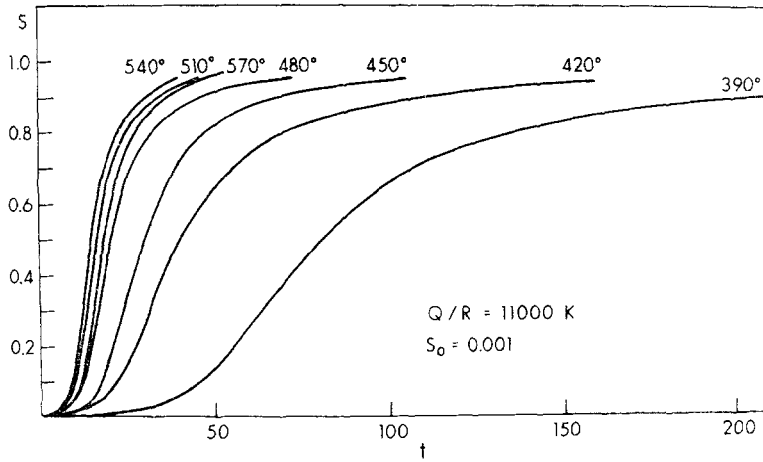


Figure 8 Homogeneous ordering. The solutions of Equation 1.

This form of free energy will give the relations:

for $T = T_c$, $F(S) = F(O)$,
 for $T > T_c$, $F(S) > F(O)$, and
 for $T < T_c$, $F(S) < F(O)$,

i.e. we will have a first-order transition with the order parameter S jumping from 1 to zero at T_c . Such a step-function for S is not a bad approximation for NiPt because for this material the equilibrium values for S (for various T) are $S \geq 0.98$ up to a few degrees from T_c where S drops to zero.

Now if we take the free energy as given in Equation 4 then for the rate of ordering (Equation 1) we get:

$$\frac{dS}{dt} = Ae^{-Q/RT} \left[1 - \exp \left\{ \frac{-V_0}{2RT} \cdot \ln \left(\frac{1+S}{1-S} \right) \right\} \cdot \left(\frac{1+S}{1-S} \right)^2 \right] \dots \dots (5)$$

Here we took $V_0 = 4RT_c$ (Bragg and Williams). We see that Equation 5 is the same as the Dienes equation except that now

$$V = \frac{V_0}{2} \ln \left(\frac{1+S}{1-S} \right) = V_0 \left(S + \frac{S^3}{3} + \frac{S^5}{5} + \dots \right) \dots \dots (6)$$

For β -brass, Dienes [9] first assumed $V = V_0S$ with $V_0/R = 1000$ K. Also he took $Q/R = 5000$ K and $\nu = 10^{13}$ sec⁻¹. This resulted in a Bragg-Williams type order-disorder transforma-

tion with $T_c (= 250$ K) and Q/R about four times smaller than the right ones. Also the plots of S versus T/T_c did not fit well with the reported values. To correct for the latter Dienes took the first two terms of the right-hand side of Equation 6 and obtained better agreement for the curve of S versus T/T_c .

To solve Equation 1 for our case we took $V(S)$ as given by Equation 6 including all the terms, i.e. we used Equation 5 for dS/dt . For the diffusion energy Q we took $Q/R = 11000$ K as found from the plot of $\ln t_{1/2}$ versus $1/T$ (Fig. 7). From the equilibrium measurements of S versus T we have $T_c = 870^\circ\text{C}$ and so V_0 is known.

Using these values, a numerical integration of Equation 1 gave the order parameter S versus time for different temperatures. The results are shown in Fig. 8. One sees that S begins from an initial value of virtually zero (we assumed $S = 0.001$ for purposes of calculation) and the curves have the familiar sigmoidal shape. The rate of ordering becomes higher and higher as one goes from 390 to 540°C, but then drops for 570°C. We thus have a maximum in the rate of ordering around 540°C.

The assumption of homogeneous ordering seems then to fit the experimental results very well except in the high temperature (570°C) cases. There is only the disturbing factor that we had to assume $Q/R = 11000$ K. A more realistic value for this parameter would be around 20000 K, and this would make the 570°C reaction rate much faster than all the other temperatures. This kind of discrepancy seems to be the case [8]

whenever this type of kinetics is applied to an ordering process.

For high temperatures if we assume that the process of ordered domain growth is the right one then we must explain the shifting of the (200), (002) superlattice lines. This cannot be accounted for by a growth process alone and we must accept the results of Southworth [7] that the nucleation does not begin with the equilibrium value of S but that there is some value S_c , which depends on the temperature, to which the nuclei are initially ordered, and that starting from this value there is a supplementary homogeneous ordering which is very quick for high temperatures and very slow for low temperatures. The data for 570°C would then appear like nucleation with perfect order only because of the high rate of the homogeneous ordering at that temperature.

To calculate S_c and see if the above reasoning is correct we proceed as follows. To have ordered domains in a disordered matrix one has to overcome a nucleation energy barrier which depends on the surface energy of the domain. We can assume that the surface energy σ is a function of S because we know that the value of c/a is a function of S . So we get [13] for the critical free energy ΔF_c and for the size of the critical nucleus n_c (number of atoms):

$$\Delta F_c = \frac{4\eta^3 \sigma^3(S)}{27(\Delta F(S))^2}; n_c = \left(\frac{2\eta\sigma(S)}{3\Delta F(S)} \right)^3 \quad (7)$$

where η is a geometrical factor depending on the shape of the nucleus.

By minimizing ΔF_c relative to S we get:

$$\frac{\Delta F(S)}{d\Delta F(S)/dS} = 2/3 \frac{\sigma(S)}{d\sigma(S)/dS} \quad (8)$$

If in this equation we put* $\sigma(S) = \sigma_0 S^2$ and $\Delta F(S)$ as given by Equation 4 then we get

$$\Delta F(S) = 1/3 \frac{d\Delta F(S)}{dS}$$

$$S = -\frac{R}{6} (T_c - T) \ln \left(\frac{1+S}{1-S} \right) S$$

This relationship will hold only for $S = S_c (< 1)$. Putting it back into Equation 7 gives:

$$\Delta F_c = -\frac{C(S)}{(T_c - T)^2} \text{ and } n_c = \frac{A(S)}{(T - T_c)^3} \quad (9)$$

*It is necessary here to make an arbitrary assumption. This relationship was chosen because in the similar alloy CuAu, the axial ratio is linearly related to S^2 , and surface energy increases with deviation of the axial ratio from unity.

*This is Christian's standard symbol.

These equations show that the nucleation barrier ΔF_c grows quickly as one approaches T_c , i.e. the nucleation process will be more difficult near T_c than at lower temperatures, and the size of the nuclei grows more quickly when approaching T_c . This conclusion is in accordance with the work of Burns and Quimby [14] who, from their own model, have calculated the rate of nucleation of ordered domains in the Cu_3Au case. (They also observed experimentally, by resistivity measurements, that ordering of Cu_3Au is slow just below T_c .)

For the nucleation rate I^{v*} one has [13]

$$I^v = N\nu \exp(-Q/RT) \exp(-\Delta F_c/RT) \quad (10)$$

where N is the number of atoms per unit volume in the disordered phase and ν is a frequency of the order of the Debye frequency. Such an equation can give us [2] a minimum for the nucleation rate but as stated above, the size of the nuclei (n_c) is also a function of temperature and varies as $(T_c - T)^{-3}$ (Equation 9).

If the homogeneous ordering for $S_c < S < 1$ inside the ordered nuclei is very quick and we have only a negligible growth of ordered domains

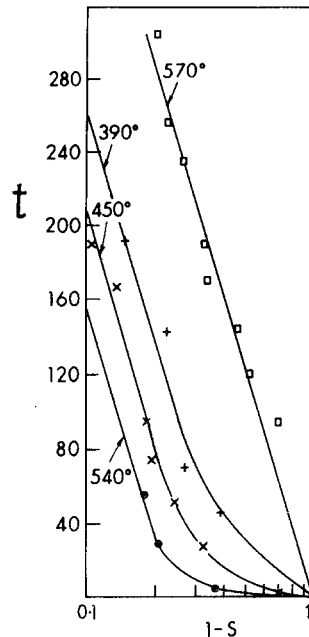


Figure 9 $\ln(1-S)$ versus the time of annealing at different temperatures. The full lines are the best fit through the experimental points.

(as in the 570°C sample) then we should have from

$$\frac{ds}{dt} \propto I^v$$

$N \propto (1 - S)$ and Equation 10

$$\frac{dS}{dt} \propto (1 - S) e^{-q/RT} \dots (q = Q + \Delta F_c).$$

For constant temperature we will then have

$$\frac{dS}{dt} = K(1 - S) \text{ where } K \text{ is a constant,}$$

$$1 - S = e^{-Kt}. \quad (11)$$

Fig. 9 gives a plot of $\ln(1 - S)$ versus t for the various samples and we see that for the 570°C annealing this plot is linear, as expected from Equation 11.

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