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Effect of thermomechanical treatment on the phase transformation in Cu–44Ni–5Cr alloy

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Cu–44Ni–5Cr alloy has been subjected to thermomechanical treatment which consisted of plastic deformation of as-quenched material by 50, 65 and 80% reduction in thickness followed by ageing in the interval of 500 to 650° C for various durations of time. Progress in age-hardening was studied by means of hardness measurement and X-ray diffraction studies. The wavelength of composition modulation and strain amplitude were measured. It was found that age-hardening was a result of interaction between spinodal decomposition and recovery processes. Prior deformation was found to enhance the kinetics of both spinodal decomposition and coarsening. It was concluded that this resulted from increased vacancy concentration and increased coherency strain in the cold-worked material.

1. Introduction

Spinodal decomposition is now well recognized as a means of strengthening by age-hardening. A number of ternary alloys based on binary copper–nickel system have been shown to strengthen by this mechanism. These include Cu–Ni–Sn [1, 2], Cu–Ni–Fe [3, 4], Cu–Ni–Si [5] and Cu–Ni–Cr [6–10] alloys. It is but natural to expect that the strength of these alloys can be greatly enhanced by subjecting them to a thermomechanical treatment rather than the conventional quenching and ageing treatment. Therefore a systematic study of the effect of thermomechanical treatment on the age-hardening behaviour of spinodal alloys is of interest, with a view to optimizing the heat-treatment conditions.

Several studies have been carried out in this direction, but the results are quite conflicting. Plewes [11] studied the spinodal decomposition of a Cu–9Ni–6Sn alloy. He reported that while cold work did not alter the wavelength of composition modulation during spinodal decomposition, it inhibited coarsening. Since cold work enhanced age-hardening, he concluded that the amplitude is raised by cold work, even though no measurements were carried out in this regard. The conclusion that spinodal decomposition does occur in materials subjected to thermomechanical treatment has been disputed by Helmi and Zsoldos [12]. In their TEM investigations, they did not see any evidence of modulated structure on ageing a previously cold-worked material. They argue that a heavily deformed matrix suppresses spinodal decomposition. This is also supported by Chandranarayanan *et al.* [13]. Studies on Cu–15Ni–8Sn alloy led Spooner and Lefevre [14] to conclude that the coarsening kinetics is unaffected by prior cold work, which they attribute to high recovery rates in their alloy. While age-hardening accelerated under prior cold work, there was no effect on the kinetics of spinodal decomposition or coarsening.

Kreye and Pech [15] have studied the effect of prior deformation on spinodal decomposition in a Cu–30Ni–2.9Cr alloy. They carried out isochronal ageing of samples previously deformed by different percentages, over a range of temperatures in the interval 400–800° C. They carried out both TEM and X-ray diffraction studies. In the latter, they observed only the presence or absence of side bands, and did not estimate the wavelength or amplitude of composition modulation. They concluded that spinodal decomposition is suppressed in samples subjected to a large amount of deformation. They attribute this to the dislocation configuration generated during deformation.

Because of these conflicting claims, it was felt necessary to carry out some further work in this direction. Spinodal decomposition is characterized by the wavelength and amplitude of composition modulation. A systematic analysis of these factors, it was felt, would help in understanding the effect of prior deformation on spinodal decomposition and coarsening. This type of analysis has not been done so far. The present investigation is, therefore, mainly based on X-ray diffraction. Earlier work [16–19] has demonstrated the success of this technique in studying the kinetics of spinodal decomposition and coarsening. As spinodal decomposition in the Cu–Ni–Cr system has been well characterized by several previous investigations, it was decided to investigate the effect of thermomechanical treatment (TMT) on spinodal decomposition in a Cu–44Ni–5Cr alloy.

2. Experimental procedure

The alloy was prepared by melting high-purity copper, nickel and chromium in an induction furnace. The

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melt was chill-cast in a cast-iron mould of size 50 mm × 38 mm × 200 mm and weighed approximately 3 kg. Chemical analysis by atomic absorption spectrophotometry showed that the alloy contained 44.28 wt % Ni and 5.4 wt % Cr, the balance being copper.

The ingot was homogenized at 1000 °C for 36 h and then quenched in water. Strips cut from this were rolled down to 1 mm thickness through several intermediate annealing steps. These were used for conventional ageing studies. Specimens cut from these were quenched from 1000 °C and then aged at 400, 500, 550, 575, 600 and 650 °C for various durations of time.

Similarly, a few strips were rolled down to 2, 2.9 or 5 mm. These were then quenched from 1000 °C and rolled down to 1 mm thickness so that they had prior deformations of 50, 65 and 80%, respectively. These were then aged at four different temperatures of 500, 550, 600 and 650 °C, for 30, 60, 90, 120 and 300 min.

Hardness was measured on a Zwick Vickers hardness tester with a load of 10 kg. The values reported are a mean of at least five readings.

X-ray diffraction studies were carried out on electropolished samples in a Jeol X-ray diffractometer using CuK_α radiation filtered with a nickel filter. The wavelength of composition modulation was estimated from these profiles using the Daniel–Lipson formula [20]. The amplitude of composition modulation was also estimated from these profiles according to the method of Ditchek and Schwartz [21] by measuring the integrated intensity under the Bragg peak and the side bands.

Samples for TEM studies were prepared by twin jet polishing (Struers equipment) at a temperature of − 30 °C. The electrolyte used was 10% perchloric acid in acetic acid and polishing was done at 20–30 V and 0.2–0.8 A cm^{-2}. The samples were examined in a Hitachi H8000 electron microscope at 200 kV.

3. Results

3.1. Conventional ageing

The variation of hardness with ageing time at different temperatures is shown in Fig. 1. In the temperature range of 400 to 575 °C the hardness is found to increase continuously with increasing ageing time, right up to the maximum ageing period of 31 h employed here. At temperatures greater than 575 °C the hardness decreases with increasing temperature. At these temperatures the hardness very quickly reaches a maximum value at which it remains constant for very long ageing periods.

A typical diffraction profile is shown in Fig. 2. Well defined side bands are observed on either side of the Bragg peak. The disposition of the side bands with respect to the Bragg peak was used in measuring the wavelength of composition modulation. Fig. 3 shows the variation of the wavelength of composition modulation with ageing time at different ageing temperatures. At temperatures up to 500 °C the wavelength was found to remain constant for all the ageing durations employed here. At 550 °C it remains constant initially, but rises gradually at longer ageing periods. At 575 °C the initial constant-wavelength regime is

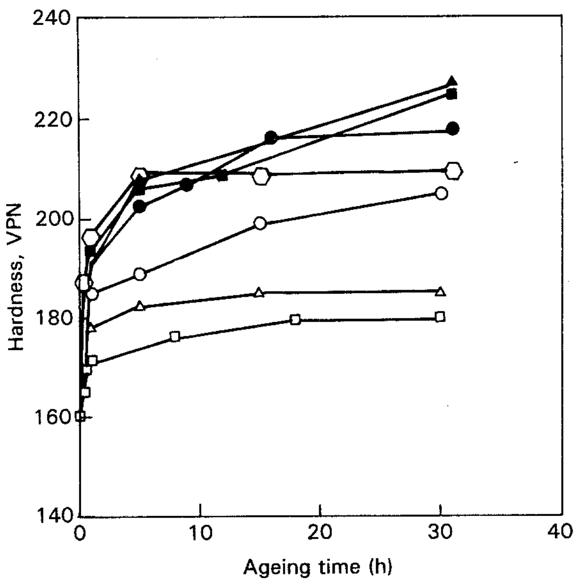

Figure 1 Variation of hardness with ageing time at different temperatures: (□) 300 °C, (△) 400 °C, (○) 500 °C, (■) 550 °C, (▲) 575 °C, (●) 600 °C, (⬡) 650 °C.

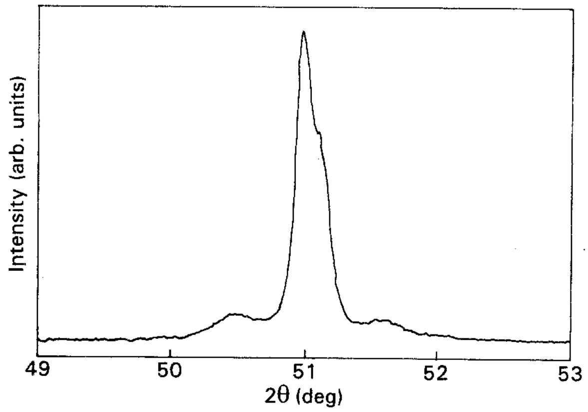

Figure 2 Diffraction profile of sample aged at 650 °C for 15 h.

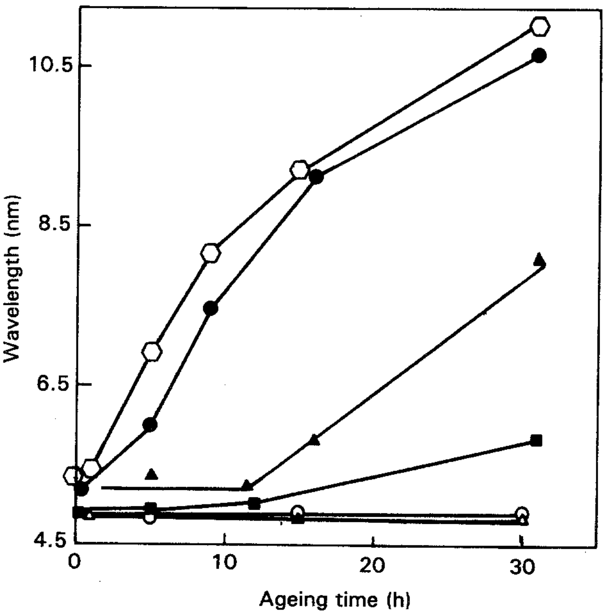

Figure 3 Variation of the wavelength of composition modulation with ageing time at different ageing temperatures: (△) 400 °C, (○) 500 °C, (■) 550 °C, (▲) 575 °C, (●) 600 °C, (⬡) 650 °C.

not clearly apparent. The wavelength increases gradually initially, and more rapidly later on. However, at temperatures of 600 °C and higher there is only a rapid increase in wavelength with ageing time.

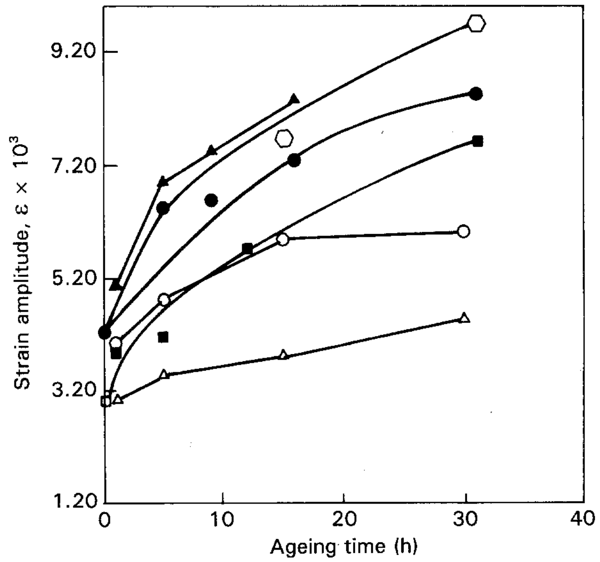

Figure 4 Variation of strain amplitude with ageing time at different ageing temperatures: (△) 400 °C, (○) 500 °C, (■) 550 °C, (▲) 575 °C, (●) 600 °C, (⬡) 650 °C.

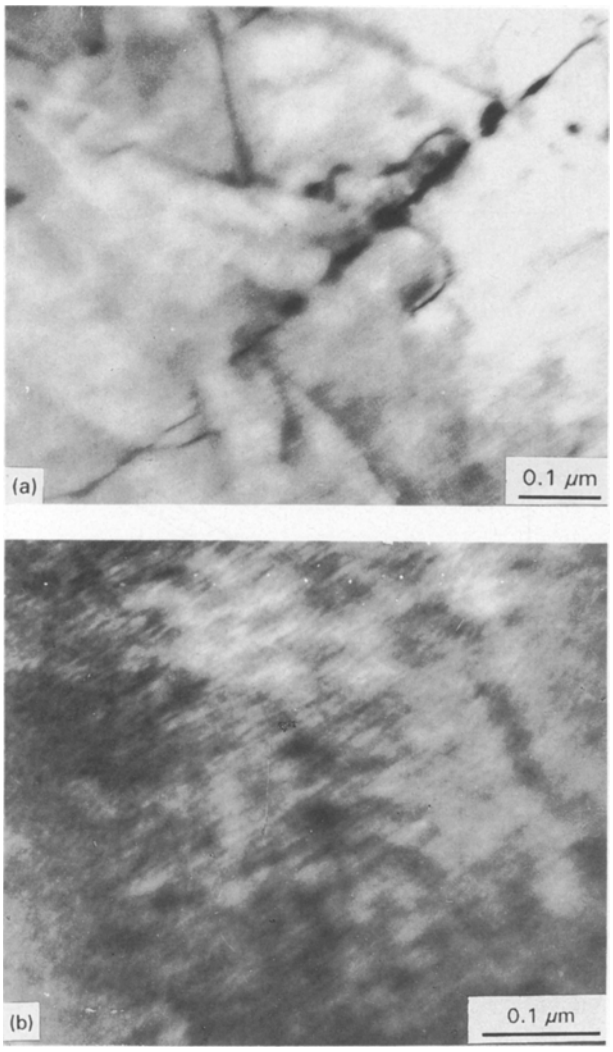

Figure 5 Microstructure of samples conventionally aged at 550 °C for (a) 30 min and (b) 5 h.

Fig. 4 shows the variation of strain amplitude with ageing time at different ageing temperatures. It is found that generally at all ageing temperatures, the strain amplitude increases with increasing time. The increase is gradual at low temperatures, but becomes faster with increasing temperature. Generally, the strain amplitude is higher for a given ageing time at higher temperatures. Some studies were also carried out at 700 °C, but in these samples it was found that, after an initial rise, the strain amplitude decreases with increasing time.

Fig. 5 shows the microstructure of the samples aged at 550 °C for 30 min and 5 h. While at 30 min only a diffuse wavy pattern could be seen, well-developed modulated structure could be seen at 5 h.

3.2. Thermomechanical treatment

The effects of prior deformation on the ageing behaviour at four different ageing temperatures are presented in Fig. 6. It can be seen that the ageing behaviour varies markedly with the amount of prior deformation as well as the ageing temperature. Generally, the hardness increases with an increasing amount of prior deformation, and decreases with increasing temperature.

Fig. 7 is a typical diffraction profile of a sample subjected to a prior deformation of 80% and then aged at 650 °C for 30 min. Side bands were clearly seen on the profiles of all the cold-worked materials. While there was a broadening of the Bragg peak, it never merged with the side band. This is unlike the results of Plewes [11], who reported that no pertinent information could be obtained from the X-ray diffraction profiles because of excessive line broadening. Spooner and Lefevre [14] also reported that broadening of the Bragg peak after 80% cold work is comparable to the angular displacement of the side-band peaks. However, the results of Kreye and Pech [15] in this regard are quite similar to those of the present investigation: the side bands were always well removed from the broadened Bragg peak. The effect of cold work on the variation of wavelength with time at the four ageing temperatures is shown in Fig. 8. It can be seen that, at all temperatures, the wavelength increases with increasing prior deformation. It is generally observed that at short ageing periods the wavelength increases with increasing ageing time. Afterwards, it reaches a plateau at which it remains until the maximum period of 5 h employed in this investigation.

The strain amplitude was also found to vary in a more complex way as compared to the conventionally aged alloys. The results are shown in Fig. 9 for different ageing temperatures. At 500 °C, low values of strain amplitude were observed at all strain levels. The strain amplitude increased very gradually with ageing time. Though there was some scatter in the values at this low ageing temperature because of small amplitudes, the trend was quite clear. The differences in strain amplitude are not great between samples of different prior deformation, and the curves are quite close to that of the undeformed material. At higher temperatures the curves shift to higher magnitudes of

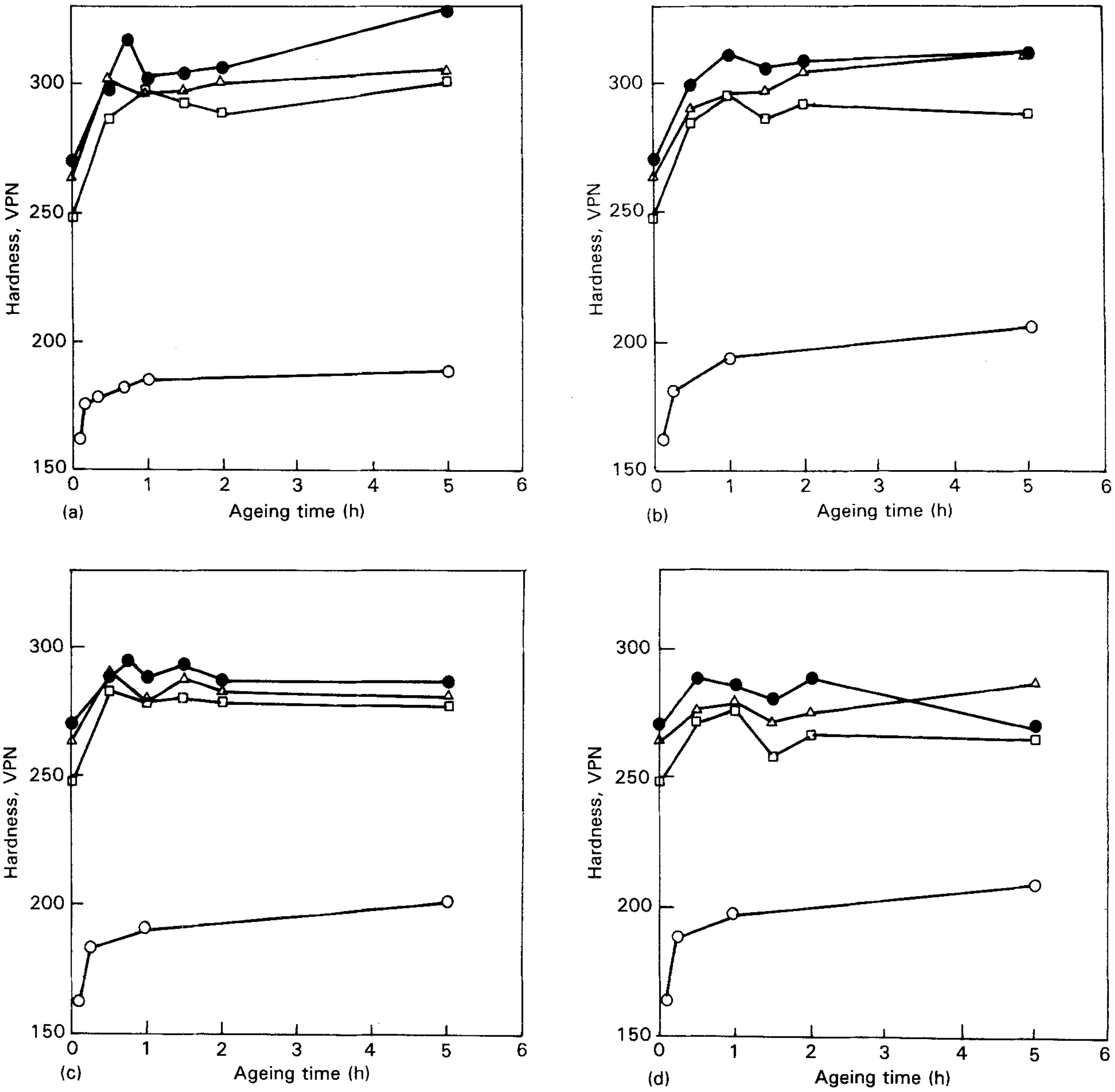

Figure 6 Effect of prior deformation on the ageing behaviour at different ageing temperatures: (a) 500 °C, (b) 550 °C, (c) 600 °C, (d) 650 °C. Prior deformation (o) 0%, (□) 50%, (△) 65%, (●) 80%.

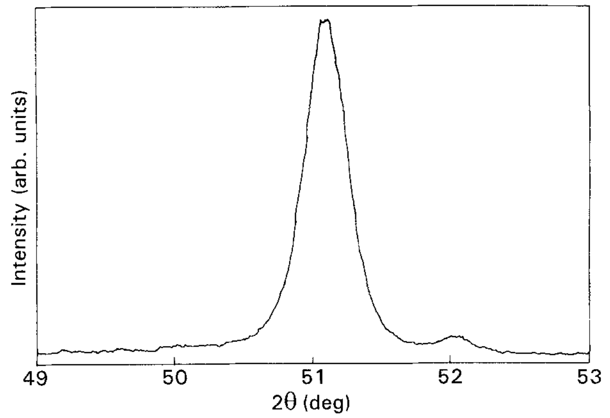

Figure 7 Diffraction profile of sample aged at 650 °C for 30 min after prior deformation by 80%.

strain amplitude. The curves also appear to reach a maximum value, beyond which the strain amplitude decreases.

Micrographs of samples subjected to a prior deformation of 80% and subsequently aged at 550 °C for 30 min and 5 h are shown in Fig. 10. The modulated structure in the sample aged for 30 min is not clearly visible, partly due to the heavy dislocation network. The one aged for 5 h shows well-developed modulated structure in pockets. There are still regions in which the modulated structure has not yet developed fully.

4. Discussion

4.1. Conventional ageing

The maximum hardness is noticed in the samples aged at 575 °C. In samples aged at lower temperatures, the time to reach such hardness would be considerably longer. Even at 575 °C, it should be noted that the hardness has not reached a peak after 31 h of ageing, the maximum period employed in the present work. At higher temperatures the peak hardness decreases with increasing temperature. A few experiments conducted at 700 °C showed that the hardness drops quickly, indicating that this temperature may be

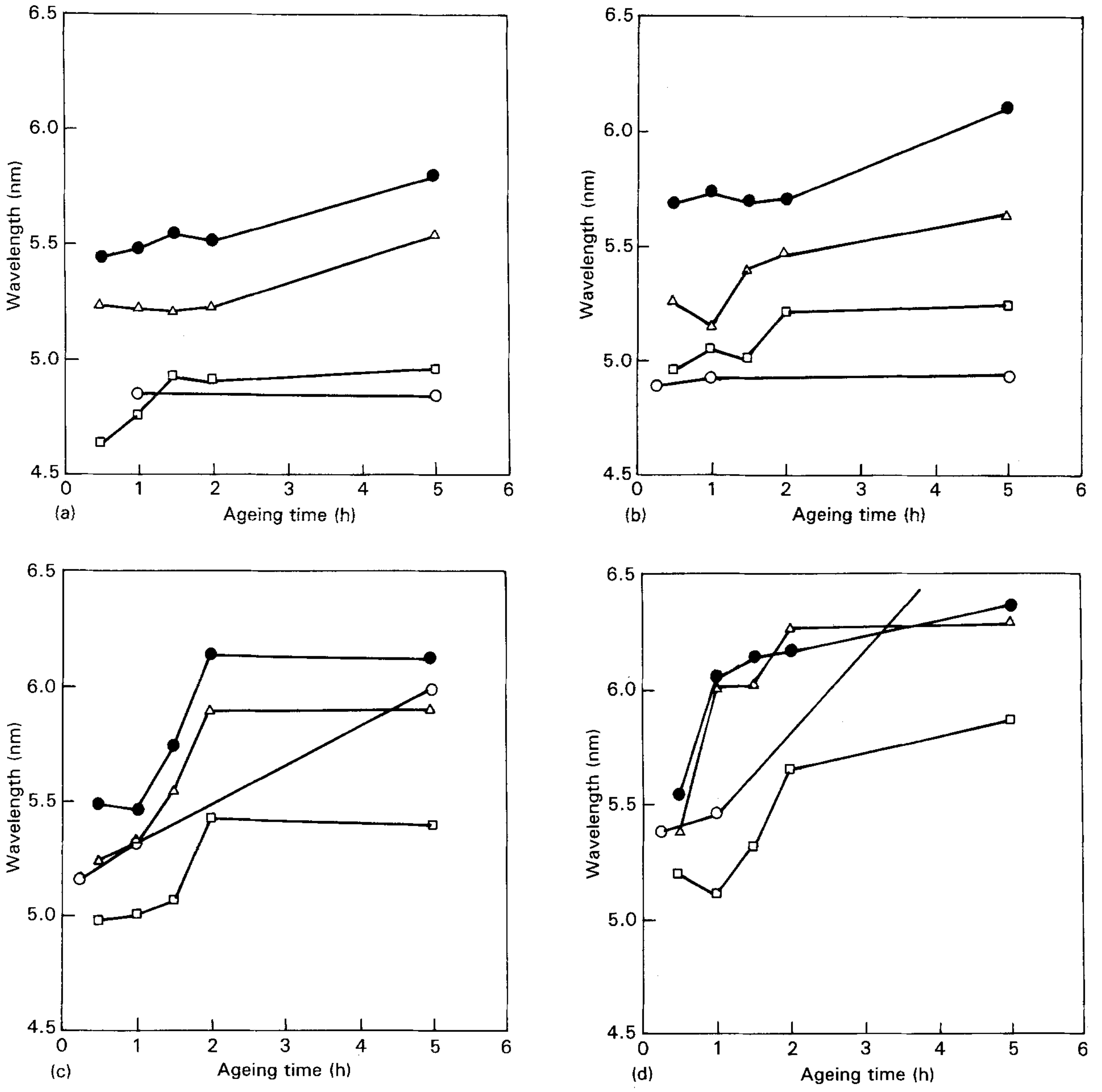

Figure 8 Effect of prior deformation on the wavelength of composition modulation for different ageing temperatures: (a) 500 °C, (b) 550 °C, (c) 600 °C, (d) 650 °C. Prior deformation (o) 0%, (□) 50%, (△) 65%, (●) 80%.

above the coherent spinodal value. Previous investigations [16, 17] on Cu–Ni–Cr alloys have shown the coherent spinodal temperature to be in the range 650–700 °C.

The variation of the wavelength of composition modulation (Fig. 3) conforms to the general pattern in alloys undergoing spinodal decomposition. It is generally agreed [22] that the wavelength remains constant during the early stages of spinodal decomposition, during which period the strain amplitude increases. At the end of this stage, the strain amplitude remains constant while the wavelength increases. This corresponds to the coarsening regime. Fig. 4 shows that during early stages the strain amplitude increases rapidly and then rises more gradually. The constant strain amplitude expected of the coarsening regime is not observed here. This may be due to the short ageing periods employed here and the sluggishness of the decomposition as equilibrium is approached. The fact that both strain amplitude and wavelength are increasing simultaneously indicates that some composition adjustment is also taking place during the coarsening regime.

It is generally expected that the saturation value of the strain amplitude decreases with increasing temperature, because the composition difference between the phases decreases. However, in the absence of any saturation value of the strain amplitude due to the short ageing periods employed, and lack of knowledge of the exact nature of the spinodal curve, no further comments can be made in this regard.

4.2. Thermomechanical treatment

The hardness measurements on the TMT specimens revealed many interesting features. On ageing at 500 °C the material previously cold-worked by 80%, the hardness increased initially. It then dropped slightly, and with continued ageing it increased again. While the initial rise and fall were observed under all conditions of TMT, the third part could be a rise, a plateau

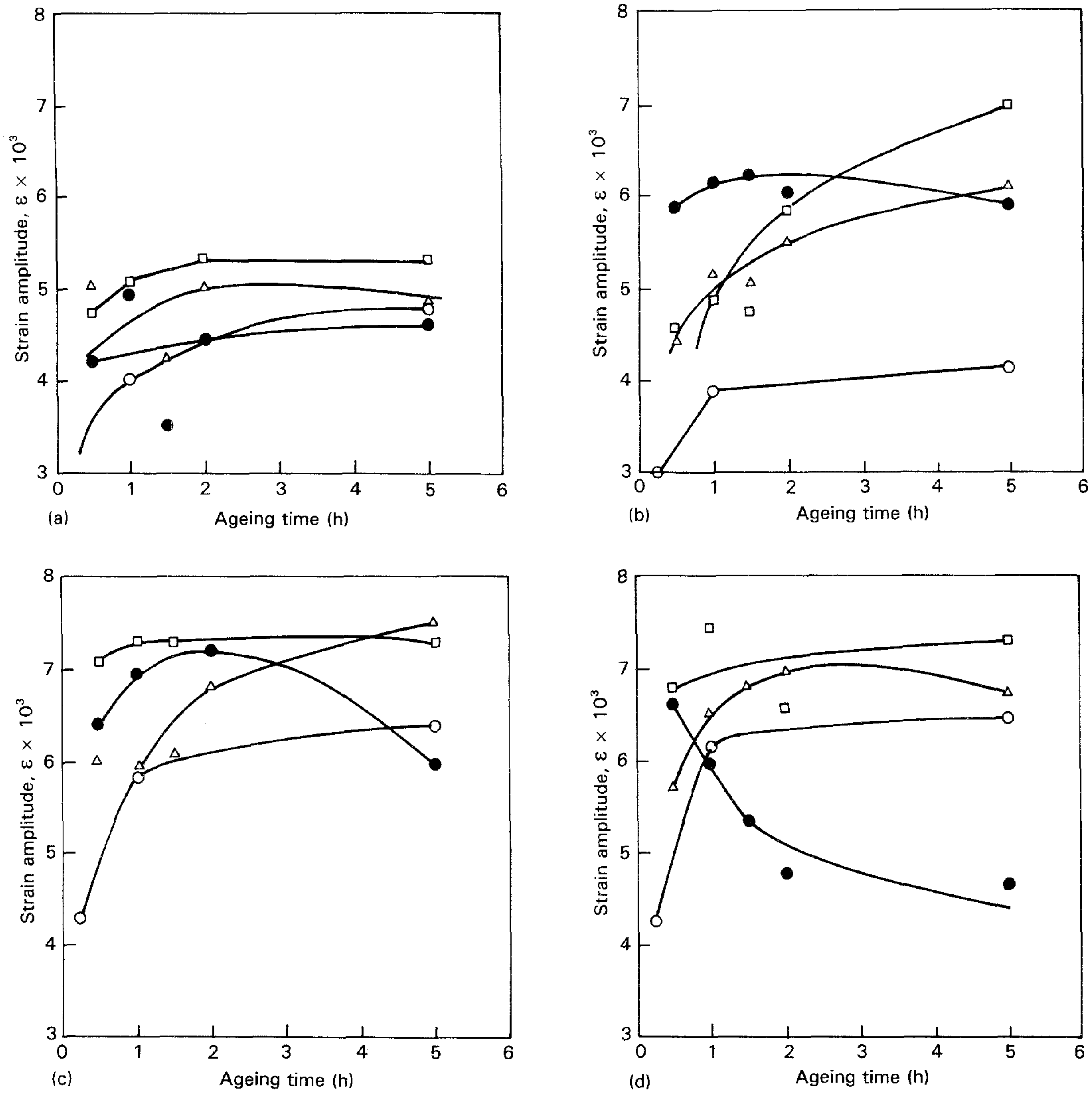

Figure 9 Effect of prior deformation on the strain amplitude for different ageing temperatures: (a) 500 °C, (b) 550 °C, (c) 600 °C, (d) 650 °C. Prior deformation (o) 0%, (□) 50%, (△) 65%, (●) 80%.

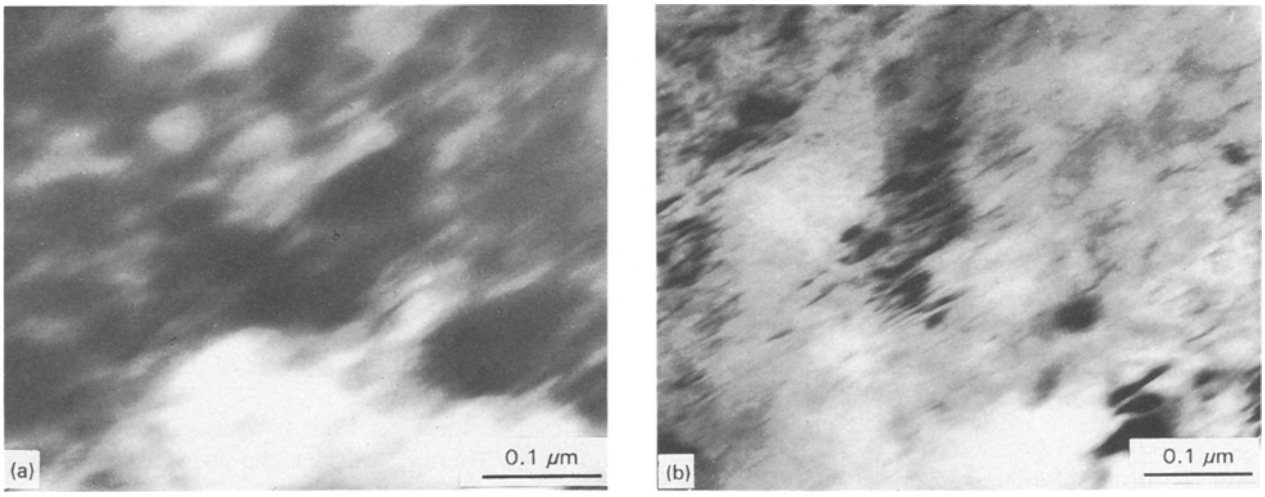

Figure 10 Microstructure of samples aged at 550 °C after prior deformation of 80% aged for (a) 30 min and (b) 5 h.

or a fall, depending on the specific combinations of prior deformation and ageing temperature. This is quite distinct from the conventional ageing where there was always a very rapid increase in early stages and a gradual rise later on. The curve was always smooth, with never a hint of rise and fall.

Fig. 11 shows a replot of hardness data from Fig. 6 for the material subjected to a prior deformation of 80% and aged at the four temperatures. The effect of ageing temperature on the nature of the hardness variation is quite clearly seen. While at the low ageing temperature of 500 °C the hardness increased quite rapidly, at the high temperature of 650 °C it dropped considerably. At the two intermediate temperatures of 550 and 600 °C, a transition could be observed: a gradual rise in the former and a plateau in the latter. This suggests that the extent of strengthening achieved through spinodal decomposition is considerably influenced by recovery processes that simultaneously occur in the cold-worked material.

During initial stages there is a rapid increase in hardness due to spinodal decomposition. After some time, recovery processes occur which lead to a drop in hardness. On further ageing, spinodal decomposition again dominates and the hardness rises once more. At low ageing temperatures only one peak is observed, and after a drop the hardness rises above the initial peak (see Fig. 6a). The greater the amount of prior cold work, the greater will be this tendency to raise the hardness (Fig. 6b). The hardness increase in the third stage is only gradual and it may just reach the value of the initial peak. At still higher temperatures (Fig. 6c and d), the hardness in the third stage will be lower than the initial peak value. There is a second smaller peak which should correspond to the end of strengthening by spinodal decomposition. This means that coherency strains, which are the principal cause of strengthening in spinodal alloys, decrease beyond this stage. The hardness after longer ageing periods will tend to be lower than that of the previously cold-worked material. A perusal of Fig. 6a to d indicates that high prior deformation and high ageing temperatures lead to a quick loss of strength during the third stage. However, at short ageing periods at all temperatures, the higher the prior deformation, the higher is the hardness. It is clear that the strain fields of the dislocations generated during cold work effectively interact with the coherency strain fields, and help in raising the strength of the material considerably.

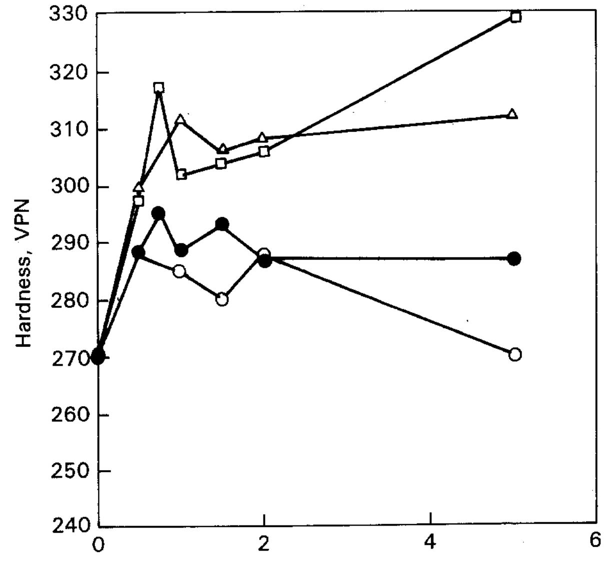

Figure 11 Variation of hardness with ageing time in 80% prior cold-worked material at different ageing temperatures: (□) 500 °C, (△) 550 °C, (●) 600 °C, (○) 650 °C.

At all ageing temperatures it is found that increased prior deformation increases the wavelength of composition modulation (Fig. 8), showing its strong influence on the kinetics of decomposition. At 500 and 550 °C, a constant initial wavelength is observed which increases later. Similar observations were also made in conventional ageing. However, two major differences are noticed. First of all, the initial constant wavelength is higher than that in conventional ageing, and it increases with increasing prior deformation. Secondly, coarsening sets in earlier than in conventional ageing. Thus it is seen that both spinodal decomposition and coarsening kinetics are accelerated by prior deformation.

Spinodal decomposition is a homogeneous transformation. This will not be affected by heterogeneous nucleating sites such as dislocations. The kinetics of the transformation depends only on the kinetics of diffusion. If diffusion is enhanced, the decomposition will be accelerated. Diffusion will increase if the vacancy concentration increases. It is now well accepted that vacancies are generated during plastic deformation, by (say) the non-conservative motion of jogged screw dislocations. However, the number of vacancies produced per unit of strain is not known to any degree of certainty. Nor is there any knowledge about the final distribution and configuration of these vacancies. The interpretation of experimental results is further complicated by the fact that dislocations that are continuously generated during plastic deformation interact with vacancies. They can also serve as sinks for vacancies.

Since vacancies are continuously generated during plastic deformation, diffusion may be expected to be enhanced. The experiments to measure this are inherently difficult because it is difficult to control a number of important parameters such as distortion of the specimen, dislocation concentration and configuration, and uniformity of strain. But there are some experimental results [23] which demonstrate quite convincingly that plastic deformation-enhanced diffusion does occur. It has been reported that diffusion is enhanced with increasing strain rate and with increasing accumulated strain. It is suggested that an increasing steady-state concentration of vacancies results from a constant generation of excess vacancies and their annealing to sinks. Dependence of diffusion enhancement on accumulated damage comes about because of the increasing number of dislocations with increasing deformation.

The dislocations can act both as vacancy sources and sinks. We may consider two possibilities:

(i) At low levels of cold work there may be a net loss of vacancies, as the vacancies generated by plastic deformation will be fewer than those mopped up by the dislocations. The kinetics of spinodal decomposition will be adversely affected.

(ii) At larger amounts of cold work there may be net gain of vacancies. The number of vacancies generated will be greater than those mopped up by the dislocations. The kinetics of spinodal decomposition will now accelerate.

The variation of wavelength with ageing time at low ageing temperatures of 500 and 550 °C can be explained in terms of the above model. We see that a critical amount of plastic deformation is needed at a given temperature to enhance the decomposition kinetics. At higher cold work and higher ageing temperatures, the reaction kinetics is found to be insensitive to cold work. At higher temperatures of 600 and 650 °C, the equilibrium vacancy concentration increases by an order of magnitude as compared to lower ageing temperatures of 500 and 550 °C. As a result, the net gain of vacancies due to plastic deformation becomes only a small fraction of the total vacancy concentration. The effect of plastic deformation therefore becomes marginal, and the difference between conventional ageing and TMT decreases.

Cahn's theory [24] of spinodal decomposition predicts that there is a composition wave, with a wave number β_m, which has the maximum amplification factor and will be in a dominating position to grow as compared to other waves. β_m does not change for short ageing durations. As ageing progresses and the amplification of the wave increases, the preferential growth of this wave keeps the wavelength constant. Such a constant wavelength has been reported not only in Cu–Ni–Cr [17, 19], but also in many other systems [4, 25, 26].

The magnitude of this constant wavelength or wave number is dependent on the ageing temperature T_a, and the following equation has been derived [22]:

$$\beta_m^2 = (T_a - T_s^*)\frac{S''}{4K}$$

where T_s^* is the coherent spinodal temperature, $S'' = \partial^2 S/\partial C^2$ and K is the gradient energy coefficient. It follows from the equation that β_m varies as the magnitude of $T_a - T_s^*$. At a given ageing temperature, if T_s^* is depressed then β_m will decrease; that is, the wavelength will increase. Since increasing cold work increases the λ_m value, one can argue that cold work tends to depress the coherent spinodal temperature.

One of the consequences of spinodal decomposition is the development of coherency strain between the phases. It has been shown [24] that the effect of elastic energy associated with coherency strain is to depress the coherent phase diagram. It has been shown in the Au–Ni system [27] that development of large elastic strain can depress the coherent spinodal temperature by as much as 600 °C. In addition to this, elastic strain associated with plastic deformation can further depress the spinodal temperature. It is pertinent to point out at this stage that Dutkiewicz [28] has shown that prior cold work leads to a depression of spinodal temperature in Cu–2 wt % Ti and Cu–4 wt % Ti alloys. Therefore, the increase of λ_m values with cold work observed in the present investigation can be attributed to the effect of elastic strain in depressing the coherent spinodal temperature.

Comparing the results for ageing at low temperatures of 500 and 550 °C on the one hand and those at high ageing temperatures of 600 and 650 °C on the other, we can see two distinct trends in the variation of wavelength with ageing time. At low temperatures there is an initial constant-wavelength regime followed by coarsening. This is very similar to that of conventional ageing. We notice that cold work has an effect similar to that of increasing temperature. Increasing cold work increases λ_m and initiates coarsening earlier.

In contrast, at higher temperatures the wavelength increases with ageing time initially and then, after about 2 h of ageing, remains constant. The initial behaviour is similar to that of conventional ageing at these temperatures where no constant-wavelength regime was noticed right from the start. Now we see that in Fig. 8c and d, the curves for 50% prior deformation are below those for conventional ageing, suggesting that the prior cold work actually retards the coarsening kinetics. At 650 °C, the curves for the two cold-worked materials of 65 and 80% deformation have almost merged into one. One can therefore conclude that rapid recovery processes occurring at higher temperatures reduce the effect of cold work accelerating the coarsening kinetics. At long durations a constant wavelength is noticed, which means that coarsening has come to a halt. At this high temperature, recovery processes can be expected to be occurring. Dislocations rearrange themselves to decrease the strain energy in the system. The stable dislocation structure that develops inhibits further coarsening. Further, the localized well of lattice defects that led to enhanced diffusion gets exhausted.

The effects of ageing temperature on the variation of wavelength with ageing time are brought out well in Fig. 12. Here, curves of Fig. 8 corresponding to 65% prior deformation are replotted. It is seen that at 500 and 550 °C there is an initial constant wavelength and then coarsening, while at 600 and 650 °C there is coarsening during initial stages, followed by a constant wavelength.

The second parameter that has been obtained from X-ray diffraction data is the strain amplitude. We are actually interested in the amplitude of composition modulation. The relation between these two is quite straightforward [21]. Hence, the terms "strain" and "composition amplitude" are used freely here to mean one and the same.

Variations of strain amplitude with prior deformation at different temperatures are shown in Fig. 9. The effect of ageing temperature on the variation of strain amplitude is brought out well in Fig. 13 for the case of 80% prior deformation. At 500 °C the strain amplitude values are very low and increase only gradually with ageing time. At 550 °C relatively high values are observed. At still higher temperature of 600 °C, one can see that the strain amplitude very quickly reaches a maximum, and drops on further ageing. But at the

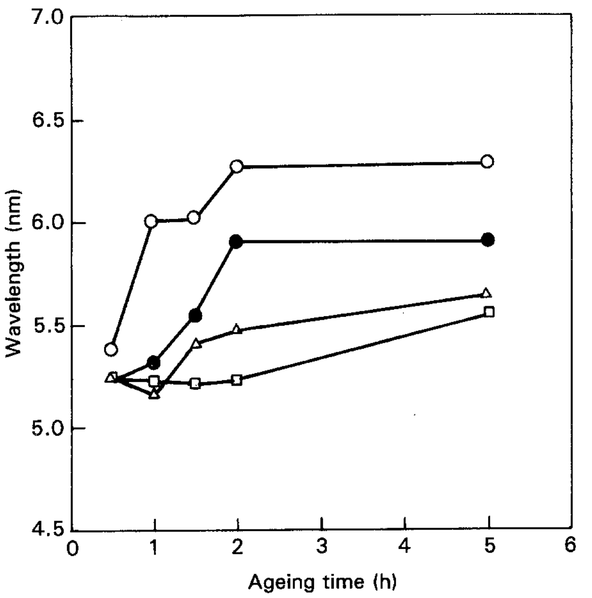

Figure 12 Variation of the wavelength of composition modulation with ageing time in 65% prior cold-worked material at different ageing temperatures: (□) 500 °C, (△) 550 °C, (●) 600 °C, (○) 650 °C.

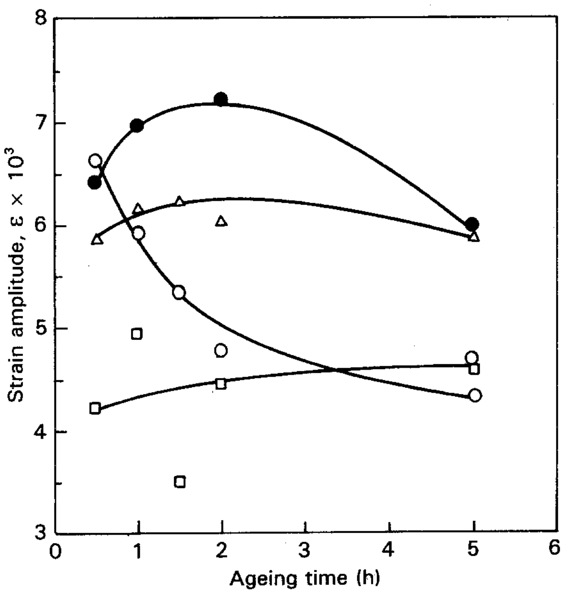

Figure 13 Variation of strain amplitude with ageing time in 80% prior cold-worked material at different ageing temperatures: (□) 500 °C, (△) 550 °C, (●) 600 °C, (○) 650 °C.

highest temperature of 650 °C, only a continuous drop is observed in strain amplitude with continued ageing. The strain amplitude has reached the maximum value within a short duration of time, less than the smallest time employed here.

An examination of Fig. 9 reveals that a similar trend as discussed above is also observed at 50 and 65% prior deformation, but the shift is more sluggish. For example, at 65% prior deformation the amplitude increases rapidly with ageing time at 550 and 600 °C, the increase being more rapid and strain amplitudes being higher at the higher temperature. At 650 °C the strain amplitude drops gradually after reaching a maximum. In other words, an effect similar to that observed at 600 °C in the material of 80% prior deformation is observed at 650 °C in a material of 65% prior deformation. At 50% prior deformation the phenomenon of dropping strain amplitude is not observed. It is observed to reach a maximum at 650 °C, and to stay there for long ageing periods.

The curves for strain amplitude generally rise to higher values as the ageing temperature is increased. This is partly due to faster kinetics of transformation at higher temperature as the strain amplitude, as already mentioned, is directly related to composition amplitude. However, we notice that strain amplitude is higher for the TMT samples as compared to the conventionally aged ones. Part of this higher amplitude can be attributed to interactions between dislocations and coherency strain fields. The fact that this is so is evident from the curves for 80% cold-worked material shown in Fig. 13. As the temperature is increased, the strain amplitude begins to decrease after a certain ageing time. The higher the ageing temperature, the earlier the decrease of strain amplitude begins. This is due to the recovery processes that set in and the rearrangement of dislocations to reduce the internal energy of the system, which includes the strain energy. This effect is observed to the greatest extent in the material cold-worked to the maximum extent and aged at higher temperature.

It is pertinent here to look at the nature of these recovery processes. Generally in spinodal decomposition, a drop in strain amplitude is associated with a loss of coherency. In Cu–Ni–Cr alloys subjected to conventional ageing, a loss of coherency has been reported [8] at these temperatures only after very long periods of ageing approaching hundreds of hours, when the wavelengths are of the order of 100 nm. However, in the present investigation a loss of coherency is observed within 5 h and that too when the wavelength is no more than 6 or 7 nm. Weatherly and Nicholson [29] have examined the mechanism of loss of coherency in precipitation-hardening alloys and have noted that migration of matrix dislocations to particle interfaces is an important mechanism. This aspect has been studied by Livak and Thomas [4] in spinodal Cu–Ni–Fe alloys, and their investigations show that the loss of coherency in these alloys indeed occurs by the above mechanism. It is argued that in the absence of sufficient matrix dislocation density, the coherency strain can activate the usual dislocation sources in the matrix and generate the necessary dislocations. This is a very slow and time-consuming process. However, if the matrix dislocation density can be raised by plastic deformation, abundant dislocations are available which can easily migrate under coherency strain to the interface of the developing particle. This accounts for the early loss of coherency in the cold-worked material. The higher the amount of cold work, the higher will be the dislocation density, and the earlier will be the loss of coherency. This is what we observe in Fig. 9. When aged at 650 °C, we see that samples deformed by 80% are rapidly losing strain amplitude, while those deformed by 50% continue to show high values of strain amplitude. Those deformed to an intermediate extent of 65% show a gradual drop. Thus the experimental results correlate well with the model of loss of coherency. The effect of temperature can be seen in Fig. 13. As the temperature is raised, dislocations are able to migrate faster to the interface under an increased thermal driving force. This accounts for the early loss of coherency, or the drop in strain amplitude at high temperatures.

At this point it is worthwhile to compare the results of the present investigation with those of earlier workers. As already pointed out, the only available report on TMT of spinodal Cu–Ni–Cr alloys is that of Kreye and Pech [15]. They have carried out X-ray diffraction studies of samples cold-worked by 10, 30, 60 and 90%, and subsequently aged at different temperatures for 1 h. They did not observe side bands in samples deformed by 90%. However, those deformed by 10 or 30% always showed them. In samples deformed by 60%, though side bands did not appear initially, they did show up later. Thus the appearance of side bands, according to them, was increasingly difficult with increasing deformation. They concluded from this that spinodal decomposition is suppressed by large plastic deformation. From the present investigation, it can be said that this is an erroneous conclusion arrived at due to insufficient data. We see that samples deformed by 80% show a large strain amplitude after ageing for only short durations. The strain amplitude drops thereafter due to migration of lattice dislocations to the interface, thereby relieving coherency strain. This occurs earlier in samples deformed to a greater extent. Thus in Fig. 9d, after ageing for, (say) 2 h, the strain amplitudes are lower for samples subjected to larger prior deformation. Therefore, while the observation of Kreye and Pech [15] is not incorrect, the inference drawn by them is not correct.

Spooner and Lefevre [14] carried out X-ray diffraction studies on samples of Cu–15Ni–8Sn alloy, previously deformed by various extent such as 20, 40, 60 and 80%, and subsequently aged for 45 min at 400 °C. They noticed a decreasing strain amplitude with increasing prior deformation. In their investigation, the study of profiles over a wider range of ageing time and temperature was inhibited by interference with the side-band profile from discontinuously precipitated DO_3 phase. However, even these limited data correlate well with the results of the present investigation. Spooner and Lefevre [14] attribute this drop to cancellation of the diffraction effect due to interaction of the strain field of modulation with the dislocation strain field. They have not explained how this can occur. However, the model proposed here, that of lattice dislocation migration to the interface, can account for this interaction of two strain fields. They further state that age-hardening is accelerated by thermomechanical treatment, but not spinodal decomposition or coarsening. The reasoning for this conclusion is not very clear. The present results show that it is not appropriate to confine kinetic studies to only one ageing temperature and only one ageing time. This may lead to incorrect inferences as explained above.

Plewes [11] studied the effect of different extents of prior deformation from 30 to 99% on the age-hardening characteristics of a number of Cu–Ni–Sn alloys. His TEM studies showed that prior deformation did not affect the kinetics of spinodal decomposition, as he did not notice a change in wavelength when compared with non-deformed samples. However, the present investigation clearly indicates an increase in λ_m with increasing prior deformation. Plewes [11] also reported that coarsening is inhibited by prior deformation. This is noticed in the present investigation also, but only at higher temperatures and longer durations. Under these conditions, matrix dislocations may migrate to the particle interface to form low-energy configurations and stabilize the interface.

A comparison of Figs 6 and 8 shows that increasing hardness correlates with increasing wavelength of composition modulation. This is observed at ageing temperatures of 500 and 550 °C. At higher temperatures, for long ageing periods a constant wavelength was observed as shown in Fig. 8c and d. Under these conditions of TMT the hardness was found to either remain stationary at the maximum value, or decrease gradually. From Cahn's model [30] it is known that the stress increases as the first power of wavelength. Thus a good correlation is noticed between hardness and wavelength. Cahn's model [30] also postulates a simultaneous dependence of strength on strain amplitude. An examination of Figs 6 and 9 shows some correlation between strength and strain amplitude. In samples previously deformed by 80% an increase in hardness as well as strain amplitude is noticed at 500 and 550 °C. However, at 600 °C the strain amplitude begins to gradually decrease after ageing for more than 2 h. Correspondingly, no increase in hardness is observed. Similarly, at 650 °C the strain amplitude is rapidly falling off, and simultaneously the hardness is also found to decrease. Similar observations can also be made at 50 and 65% prior deformation.

It is interesting to observe that, at all levels of prior deformation, the hardness increment from the as-cold-worked condition to the first peak is more or less the same, and this decreases with increasing ageing temperature. Therefore, this increment can be assigned only to spinodal decomposition. This will result in an increase in strength over and above that of the cold-worked state. At a given ageing temperature this will be same, irrespective of the amount of prior deformation.

5. Conclusions

Our systematic X-ray diffraction studies, at different ageing temperatures and times on samples deformed by different extents, have cleared up many of the contradictions in the literature. It is observed that prior deformation has a profound effect on the transformations that occur during ageing. Results concerning the wavelength as well as strain amplitude reveal that both spinodal decomposition and coarsening kinetics are enhanced by prior deformation. Increasing prior deformation has an effect similar to increasing ageing temperature. The following conclusions can be drawn from the present investigation:

1. The alloy Cu–44Ni–5Cr shows all the characteristic features of spinodal decomposition under conventional ageing.

2. The variation of hardness with ageing time in the thermomechanically treated samples shows fluctuations which arise from interactions between spinodal decomposition and recovery processes.

3. Enhancement of the kinetics of spinodal decomposition and coarsening occurs in the thermomechanically treated samples because of enhanced vacancy concentration.

4. At a given ageing temperature, λ_m is found to increase with increasing cold work. This arises because of the addition to the coherency strain energy from the elastic strain of plastic deformation, which leads to a lowering of the coherent spinodal temperature.

5. At higher ageing temperatures, the coarsening process is halted due to the recovery processes which stabilize the interfacial dislocation structure.

6. A decrease of strain amplitude is noticed in samples of higher cold work at higher ageing temperature, possibly resulting from a rearrangement of dislocation structure to lower the strain energy of the system.

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