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Characteristics of the continuous coarsening and discontinuous coarsening of spinodally decomposed Cu-Ni-Fe alloy

H. X. LI*, X. J. HAO, G. ZHAO, S. M. HAO
School of Materials and Metallurgy, Northeastern University, Shenyang 110006, People's Republic of China
E-mail: hxli@mail.neu.edu.cn

The spinodal decomposition and coarsening reaction of a 45Cu-30Ni-25Fe alloy aged with and without prior 75% cold rolling have been studied by Vickers hardness tester, X-ray diffraction, optical microscope, and scanning and transmission electron microscopes. Spinodal decomposition took place in the alloys aged in the temperature range of 600–950°C without prior deformation, and then spinodal structure in these alloys would coarsen only continuously. Spinodal decomposition and continuous coarsening reaction of spinodal structure took place in the alloys aged at lower temperature with prior deformation. This process was corresponding to recovery of spinodal structure in the deformed alloys. Discontinuous coarsening reaction of spinodal structure would also take place in the alloys aged at higher temperature with prior deformation. This process was corresponding to recrystallization of spinodal structure in the deformed alloys.

1. Introduction

Solid solutions decomposed by the spinodal mechanism do not need to overcome the activation energy barrier for nucleation, and the spinodal wavelengths could be controlled in nanometer grade [1] so that it might be possible to make nanometer two-phase materials by spinodal decomposition [2]. In elastically anisotropy systems such as face-centred-cubic Cu-Ni-Fe alloys, spinodal decomposition occurs along the elastically 'soft' directions, and periodic coherent structure composed with alternative copper rich and (Fe-Ni) rich phases formed to minimize the elastic strain energy of the two-phase microstructure. Especially in alloys whose compositions lie at the center of the miscibility gap, both phases formed by spinodal decomposition have almost the same volume fraction, and the thickness of an individual platelet is half of the wavelength [3]. The coherent platelets lose coherency as interfacial dislocations from aging [4–6].

The interfaces of the spinodal structure are usually coherent or semicoherent [4]. Plastic deformation to some extent could change the morphology and the interface structure of the spinodal structure, and equiaxed two-phase grains could form [7]. However, plastic deformation could also effect the stability of the spinodal structure [8, 9] so that some new attention has been given to the stability of the spinodal structure recently [10–12]. The spinodal structure in alloys with plastic deformation coarsens by a new regularity, and this coarsening regularity has not been clear yet.

The present work has found that the spinodal structure coarsens by two kinds of mechanism, named continuous coarsening (i.e. the spinodal wavelength increases uniformly and continuously) and discontinuous coarsening (i.e. highly coarsened cellular morphology forms by nucleation and boundary-migration to consume the finer spinodal matrix). The comparative analysis of the characteristics of these two coarsening modes has been carried out in the present work.

2. Experimental procedure

The alloy was prepared by melting 99.9% purity Fe, 99.95% electrolytic Cu, and 99.9% electrolytic Ni and then casting into a cold iron mold in a ZG-10 vacuum induction furnace protected by argon. The ingot weighed 5 kg. The nominal composition 45Cu-30Ni-25Fe (at%) was designed according to the phase diagram [13], and the alloy was expected to be with equal volume fractions of Cu rich phase and (Fe-Ni) rich phase.

The ingot was forged into 20 mm × 20 mm in cross section and followed by solution treatment at 1100°C for 48 h and then quenching in water. Strips cut from the block were cold rolled by 0% or 75% reduction, and then aged at 600, 700, 800, 900, 950°C respectively. Some deformed strips were step-aged. All the heating processes were carried out in a vacuum furnace and the vacuum degree was about 1 Pa.

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[*] Author to whom all correspondence should be addressed.

Hardness was measured on a Vickers hardness tester with a load of 5 kg. The value reported was a mean of at least four readings.

X-ray diffraction studies were carried out on a Rigaku D/max-YA x-ray diffractometer using a rotated copper target.

The microstructures were characterized by Versamet-2 optical microscope (OM), Philips-XL 30(FEG) scanning electron microscope (SEM) and Philips-EM400T transmission electron microscopy (TEM). The etchant for the OM and SEM microscopy was 2 parts HNO_3, 1 part CH_3COOH and 1 part H_2O. The electropolishing solution for the TEM sample preparation was 25% perchloric acid-methanol solution. The foils were examined at 100 kV.

Misorientation for grain boundary was measured on TEM by μ-diffraction [14] because the grains were small and not suitable for selected area diffraction (SAD).

3. Results and discussion

3.1. Structural characteristics of the continuous coarsening and discontinuous coarsening of spinodal structure

For the non-deformed alloy aged below 950°C, spinodal decomposition took place and alternative copper-rich and (Fe-Ni) rich phases formed along the elastically soft cube directions so that tweed pattern structure formed. As aging proceeded, only continuous coarsening occurred in the spinodal structure. The spinodal wavelength increased continuously, but the typical morphology of the tweed pattern hasn't changed. The spinodal wavelength in the alloy aged at 600°C for 50 h after solution treatment increased to about 40 nm (Fig. 1a); and the spinodal wavelength in the alloy aged at 600°C for 100 h after solution treatment increased to about 60 nm (Fig. 1b). The SAD pattern along [100] direction of the alloy treated as Fig. 1b showed that only one set of fcc pattern existed and the spots elongated along two $\langle 001\rangle$ directions (Fig. 1c). This SAD pattern revealed that the morphology of the decomposition products was rod-shaped, and the particles precipitated on $\{001\}$ planes and aligned along $\langle 001\rangle$ directions—the elastically soft directions in cubic crystals. The spinodal wavelength in the alloy aged at 900°C for 2 h after solution treatment coarsened to about 180 nm, but the morphology of the tweed pattern hasn't changed (Fig. 1d). The SAD pattern corresponding to the alloy treated as Fig. 1d was the same as Fig. 1c. The copper rich phase appeared as the lighter colored region and the other was (Fe-Ni) rich phase in TEM [4].

Spinodal decomposition first took place in the alloys aged in the temperature range of 600–950°C after solution treatment and cold rolling by 75% reduction, then the spinodal structure in these alloys continuously coarsened. The morphology of the spinodal structure in these alloys was no longer the tweed pattern, but changed into almost equiaxed structure (Fig. 2a).

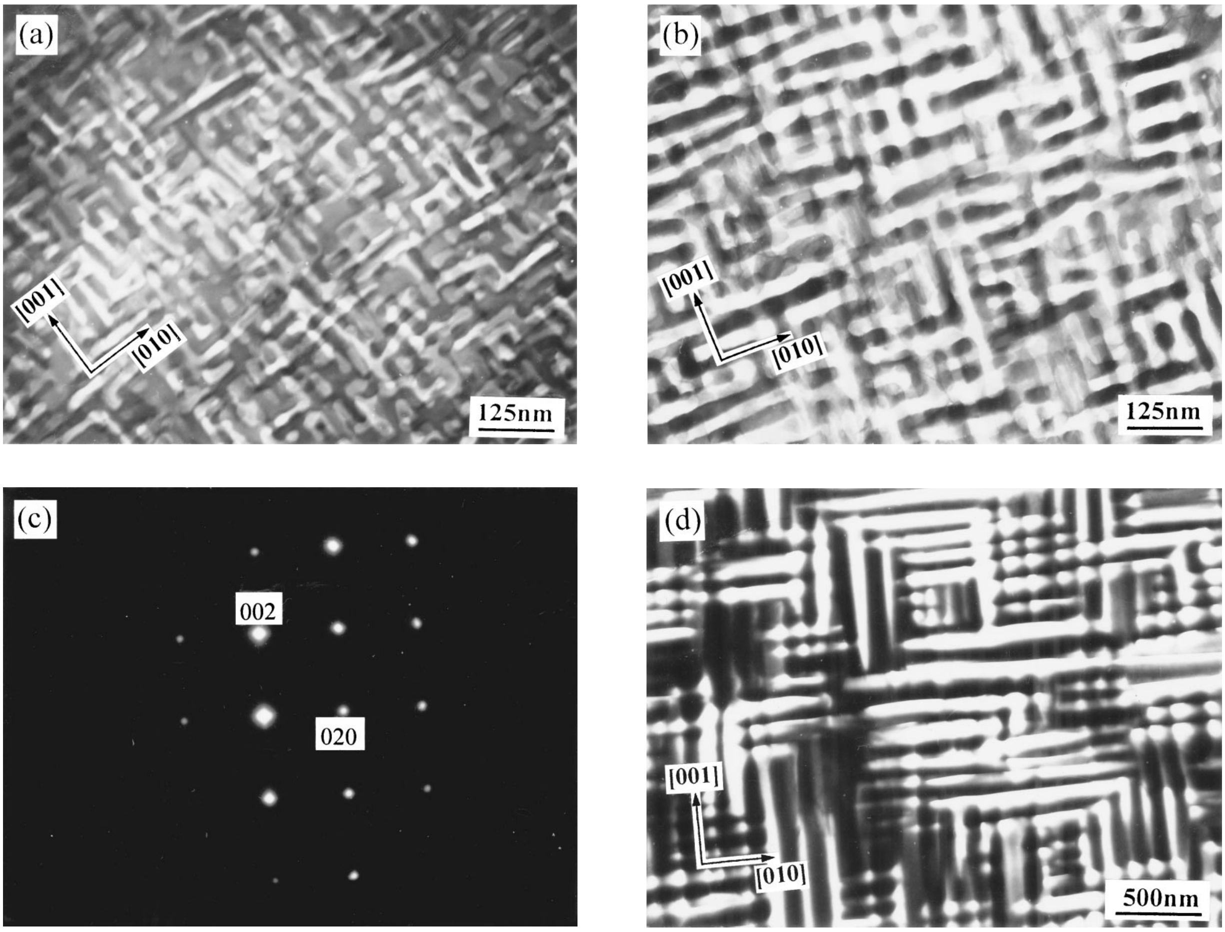


Figure 1 Microstructure of the alloy directly aged after solution treatment (TEM): (a) aged at 600°C for 50 h, (b) aged at 600°C for 100 h, (c) SAD pattern along [100] direction of sample treated as (b), (d) aged at 900°C for 2 h.

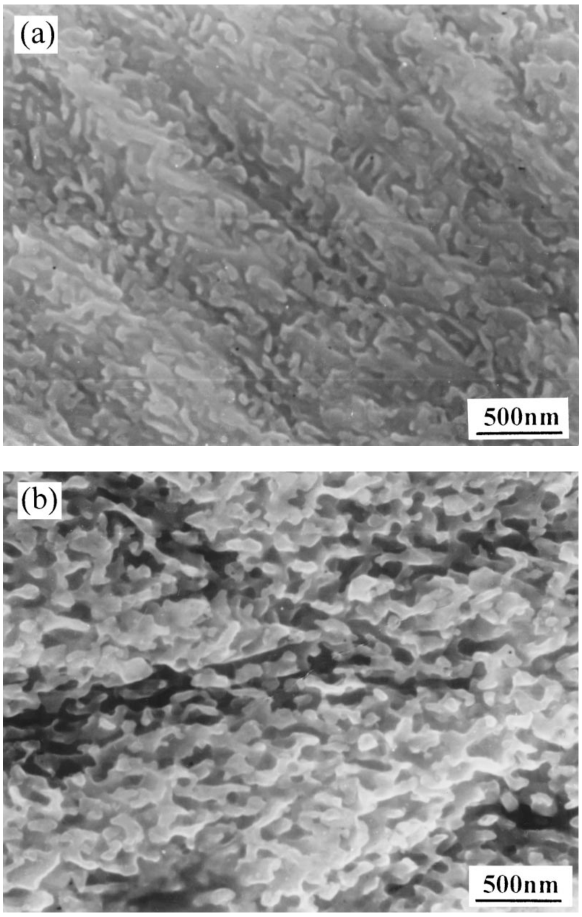


Figure 2 Microstructure of the alloy step-aged after cold rolling by 75% reduction (SEM): (a) aged at 600°C for 50 h after cold rolling by 75% reduction, (b) aged at 700°C for 2 h then at 800°C for 1h after treatment (a).

With the increase of aging time and temperature, the grain size of spinodal structure increased uniformly and the morphology became more equiaxed (Fig. 2b), i.e. the continuous coarsening reaction was enhanced. The spinodal structure in the alloy aged at 600°C for 100 h with prior deformation coarsened only by the continuous mode, but the spinodal structure in the alloys directly aged above 700°C after deformation would also coarsen discontinuously. However, it was noticeable that the spinodal structure wouldn't coarsen by discontinuous mode until 800°C if spinodal structure could continuously coarsen sufficiently by increasing aging temperature slowly or step by step (also see Fig. 2b). It was because sufficient continuous coarsening decreased the driving force for the discontinuous coarsening of spinodal structure. The structural characteristics of continuous coarsening in the alloys aged with prior deformation were that the two-phase grains were uniform and almost equiaxed.

The spinodal structure in the alloys directly aged above 700°C after deformation would also coarsen discontinuously after it continuously coarsened to some extent. The dominant driving force for discontinuous coarsening was the reduction in total interfacial energy of highly dispersive interphase. The nucleus of discontinuous coarsening reaction formed at slip bands (Fig. 3a), then developed in a cellular morphology by boundary migration to consume the fine equiaxed matrix spinodal (Fig. 3b). Measured by μ differaction analysis, the average angle of misorientation for moving boundaries was about 17.14°, and the average angle of misorientation for fine matrix spinodal was about 3.18°, i.e. discontinuous coarsening cell grew by high-angle boundary migration and consumed fine spinodal 'subgrains'. Interfacial dislocations regularly aligned on interfaces of $\gamma_{\mathrm{Cu}}/\gamma_{\mathrm{FeNi}}$ lamellae in discontinuous coarsening cell (Fig. 3c), so that the interfaces were semicoherent. The average dislocation spacing D in Fig. 3c was measured as $\sim$360Å. Structural parameter $a_{(\mathrm{av})}$ was calculated as 3.59Å from x-ray diffraction pattern. Using the formula $\delta = a/D$, the mismatch parameter δ could be obtained as $\sim$1%. As aging time increased, the morphology gradually changed into nearly lamellar structure (Fig. 3d).

It was also found that the discontinuous coarsening reaction was enhanced by aging temperature and made microstructure nonuniform.

3.2. Characteristics of hardness change in the continuous coarsening and discontinuous coarsening of spinodal structure

Spinodal decomposition took place in the alloys aged in the temperature range of 600–950°C direclty after solution treatment, and then spinodal structure in these alloys would coarsen continuously. The hardening characteristic of these alloys was consistent with the regularity of age-hardening alloy. During isothermal aging, hardness increased to a peak value with aging time and then dropped. The time to the peak strength and the peak strength value decreased with aging temperature (see Fig. 5).

The age hardening response of the alloy with prior 75% cold rolling was shown in Fig. 4. It was shown that these curves could be divided into two groups according to the tendency of hardness decreasing with aging time. One group included two hardness curves of the alloys aged at 600°C and 700°C with prior deformation. Hardness of this group decreased slowly and kept a high value until aging for 100 h. Hardness also reached a peak value when the deformed alloy aged at 600°C for 2 h. The changes in hardness of these deformed alloys were mainly caused by continuous coarsening reaction of spinodal structure.

The other group included the hardness curves of the alloys aged at 800, 900, 950°C with prior deformation. Hardness of this group decreased fast and reached very low value after aging for 100 h. Finally, the hardness of these alloys gradually reached the same value. It was because the main reaction in these alloys was discontinuous coarsening of spinodal structure.

Comparing the aging hardness of the alloys with and without prior deformation, we can see the hardening characteristics of the continuous coarsening reaction and discontinuous coarsening reaction more clearly. The results were shown in Fig. 5. The peak strength of the alloys aged at 600°C with and without prior deformation was caused by spinodal decomposition. Prior deformation decreased the time to the peak strength, and the following decrease in hardness with aging time

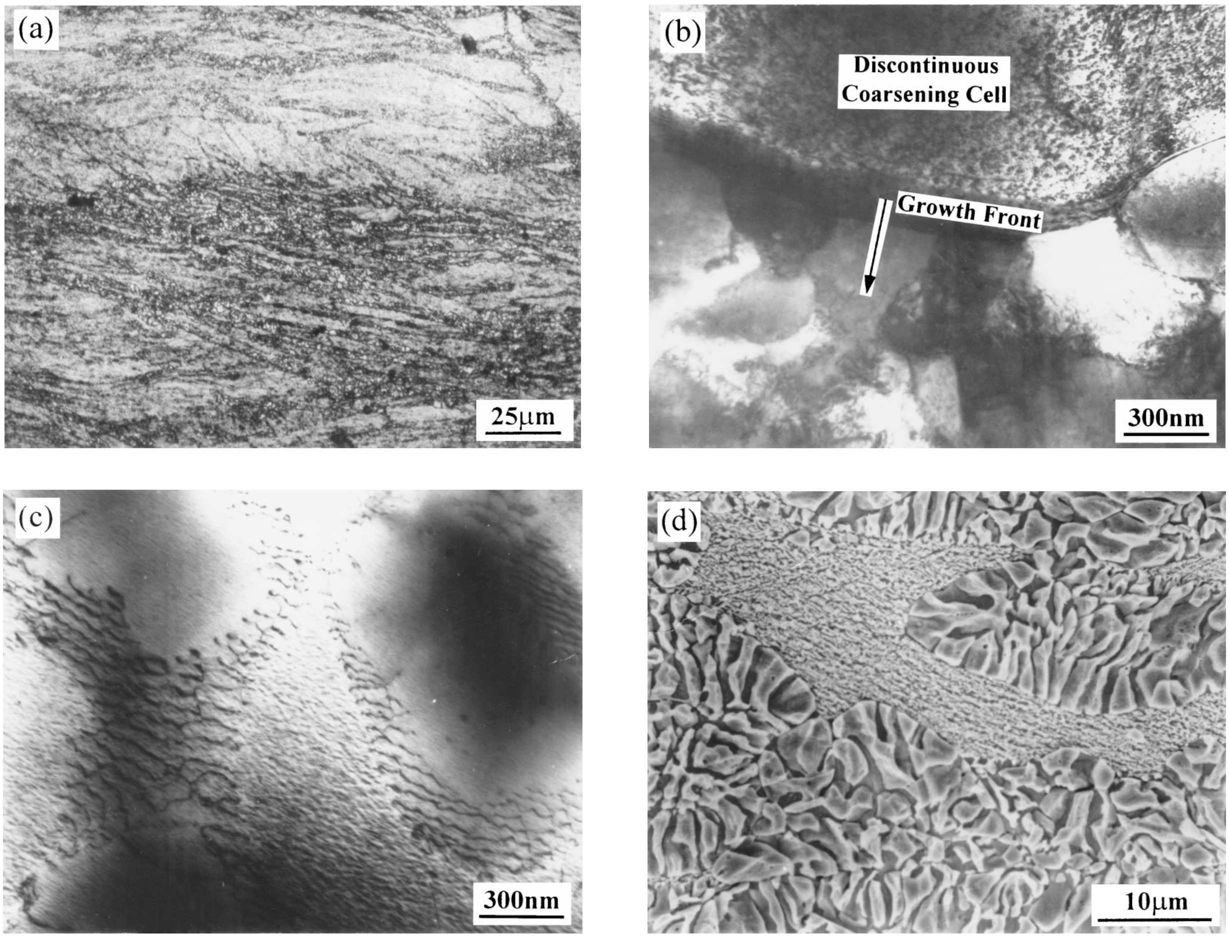


Figure 3 Microstructure of the alloy aged at 900°C after cold rolling by 75% reduction: (a) aged at 900°C for 2 h (OM), (b) (c) aged at 900°C for 8 h (TEM), (d) aged at 900°C for 24 h (SEM).

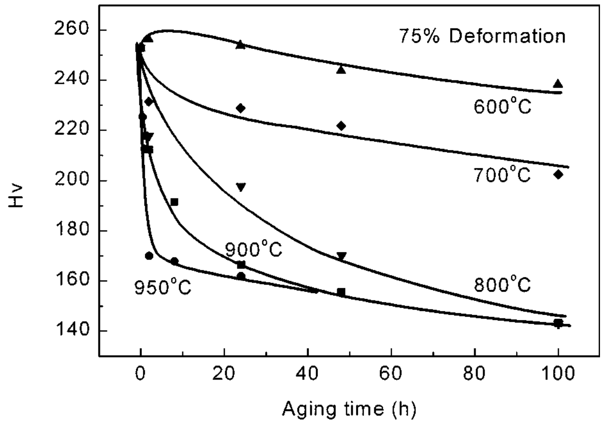


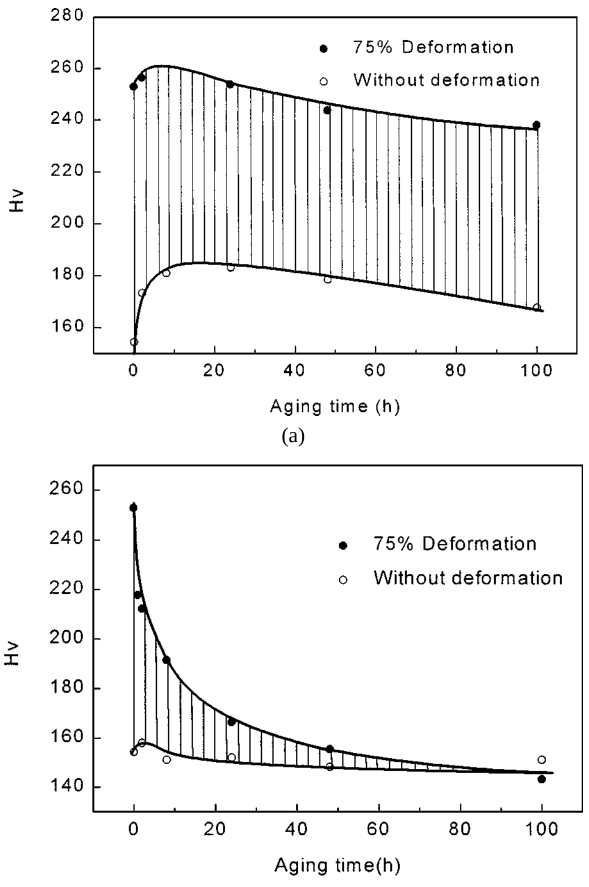
Figure 4 Variation of hardness with aging time for the alloy with prior 75% cold rolling.

was caused by continuous coarsening reaction of spinodal structure. Most of the defects induced by deformation have been kept (Fig. 5a). The hardness of the alloy aged at 900°C with prior deformation didn't show a peak strength. It was because the reaction rate of discontinuous coarsening at this aging temperature was fast and the defects induced by deformation decreased rapidly. The defects induced by deformation almost disappeared after the alloy being aged at 900°C for 80 h, then the hardness of the alloy with prior deformation was the same as that of the non-deformed alloy (Fig. 5b).

According to the structural and hardening characteristics of these alloys, continuous coarsening reaction was corresponding to the recovery process of spinodal structure in the deformed alloy, and discontinuous coarsening reaction was corresponding to the recrystallization process of spinodal structure in the deformed alloy.

3.3. Activation energies of continuous coarsening and discontinuous coarsening of spinodal structure in the alloy with prior 75% cold rolling

The activation energy was calculated using the reaction rate theory by employing Arrhenius type equation to describe the age hardening process of the alloys with prior 75% cold rolling. The aging time for hardness to drop by 10% (i.e. the time when spinodal structure in the alloy hasn't coarsened discontinuously yet) was plotted against reciprocal of absolute temperature (Fig. 6). Activation energy calculated from the slope of the straight line was obtained as 160 kJ/mol. At this time, the main reactions in the deformed alloys were spinodal decomposition and continuous coarsening of spinodal structure. So this activation energy could be interpreted as the one for continuous coarsening of spinodal structure. This value was smaller than that for interdiffusion in γ-phase of Cu-Ni-Fe alloy, because diffusion could occur along dislocations induced by deformation, making the energy needed decrease.



(a)

(b)

Figure 5 Hardening characteristics of continuous and discontinuous coarsening reactions of spinodal structure in alloys: (a) hardness of the alloys aged at 600°C with and without prior 75% cold rolling, (b) hardness of the alloys aged at 900°C with and without prior 75% cold rolling.

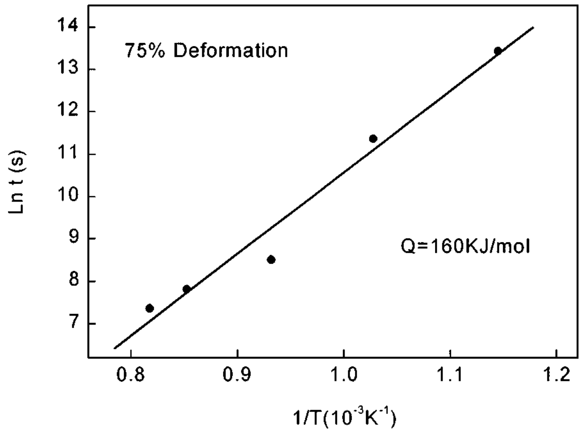


Figure 6 Effect of aging temperature on time for hardness to drop by 10% in the alloy with prior 75% cold rolling.

Similarly, according to the aging time for hardness to drop by 35% (i.e. the time when spinodal structure in the alloy has fully coarsened discontinuously), the activation energy calculated from the slope of the straight line was obtained as 206 kJ/mol. This value agreed well with the activation energy calculated from the volume fraction transformed by discontinuous coarsening mode (194 kJ/mol) [8]. It was shown that the mechanism of decrease in hardness was the discontinuous coarsening reaction in spinodal structure.

The spinodal structure in the alloy aged at 900 °C for 100 h without prior deformation didn't coarsen discontinuously. After additive energy was introduced by deformation, the nucleus of the discontinuous coarsening reaction formed at high energy zones (such as slip bands) in the alloy aged at 900°C for 2 h with prior deformation. And eventually the nucleation and growth process finished. It was shown that the energy for discontinuous coarsening reaction of spinodal structure was higher than the one for continuous coarsening reaction. This is in consistence with the experimental result.

4. Conclusion

(1) Spinodal decomposition took place in the alloys aged in the temperature range of 600–950°C without prior deformation, and then spinodal structure in these alloys would coarsen continuously in 100 h of aging time. The morphology of spinodal structure in these alloys was tweed pattern.

(2) Spinodal decomposition and continuous coarsening reaction of spinodal structure took place in the alloys aged at lower temperature with prior deformation. The rate of coarsening reaction increased with aging temperature. The morphology of spinodal structure was equiaxed. Most of the defects induced by deformation have been kept. The process was corresponding to recovery of spinodal structure in the deformed alloy.

(3) Spinodal decomposition, continuous and discontinuous coarsening reactions of spinodal structure took place in the alloys aged at higher temperature with prior deformation. The structure was nonuniform. The hardness was dependent on the extent of discontinuous coarsening transformation. Finally, the defects induced by deformation all disappeared. This process was corresponding to recrystallization of spinodal structure in the deformed alloy.

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