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Microstructure and Properties of a Cu-Ni-Cr Spinodal Alloy

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ABSTRACT

A commercial Cu-28% Ni - 2.8% Cr alloy has been heat treated to produce spinodal structures. Conventional transmission electron microscopy (TEM) and diffraction have been used to study the spinodally decomposed product and to measure the wavelengths in the specimens. It is found that the coarsening of coherent particles obeys the relation $\lambda \propto t^{1/3}$ at 700°C and $\lambda \propto t^{1/4}$ at 600°C. Loss of coherency is observed only when aging at 700°C and $\lambda \sim 1000\text{\AA}$, when interfacial dislocations with $\vec{b} = a/2 \langle 110 \rangle$ are created after which the coarsening rate is accelerated. Tensile tests were performed to measure mechanical properties of the aged samples, and the fracture surfaces were examined by scanning electron microscopy. The correlations of microstructural changes and mechanical properties are discussed.

INTRODUCTION

The object of this research is to investigate experimentally the spinodal characteristics of an alloy and then correlate the mechanical properties with the changes in microstructure during spinodal decomposition and particle coarsening. Cu-Ni-Cr was chosen particularly for its commercial importance as an alloy of excellent strength and corrosion resistance in marine environments.¹ The constitutional studies by Meijering et al.² have shown that there is a miscibility gap in the face-centered cubic phase portion of the Cu-Ni-Cr system, although binary Cu-Ni alloys are completely miscible (Fig. 1). Badia, Kirby, and Mihalisin³ have studied the strengthening during continuous cooling of Cu-Ni-Cr alloys containing 20 to 45% Ni with up to 4% Cr. Many of these experimental observations were in accord with the theoretical calculations of Huston, Cahn and Hilliard⁴ for spinodal decomposition during continuous cooling.

From the literature,¹ it was concluded that the present Cu-Ni-Cr alloy would undergo spinodal decomposition when aged at temperatures below 760°C, with the formation of Cu-rich and Ni-Cr rich phases. These phases are both face-centered cubic, and have lattice parameters after heat-treating at 750°C of 3.603Å and 3.571Å respectively.^{2,3}

In this research, the alloy was quenched and aged at two temperatures (600°C and 700°C) to produce the spinodal structure, and the changes in microstructure and wavelength with aging time were followed by transmission electron microscopy and diffraction. The mechanical behavior of the spinodally decomposed and aged alloys was then

investigated and correlated to the microstructure changes.

EXPERIMENTAL PROCEDURES

Specimens were kindly provided by International Nickel Company and chemical analysis done at the Paul D. Merica Laboratory gave the following results, expressed in weight%:

Ni - 28.9 %	Ti - 0.051%
Cr - 2.84 %	Si - 0.091%
Mn - 0.55 %	Fe - 0.32 %
Zr - 0.22 %	Cu - balance
C - 0.014%	

The alloy was encapsulated in evacuated quartz tubes, homogenized at 1100°C for 72 hours, quenched into ice brine and cold rolled to 10 mils (~ 254 μ m) thickness for transmission electron microscope specimens.

After cutting and machining, the various experimental specimens were annealed in quartz tubes filled with purified argon at 1100°C for two hours and quenched again in ice brine.

Specimens were subsequently aged at 700°C and 600°C for various times from 10 min. to 808 hours.

The heat-treated specimens were chemically polished in a solution of 3 parts of HNO₃ and 1 part of HF at room temperature, to a thickness of 3-5 mils, and mechanically polished on (600) grit emery paper before final thinning for electron microscopy. Thin foils were prepared by jet-electro polishing with the following solutions and conditions:

solution: 125 ml nitric acid and 375 ml methanol
condition: temperature: -20°C to -25°C (cold methanol was used
as a cooling bath)
polishing voltage: 20V (DC)

Specimens were then observed in a Siemens IA Elmiskop and a Philips EM 301 transmission electron microscope operating at 100KV.

For tensile test specimens, the heat-treated alloys were first machined into flat tensile specimens and then were tensile pulled in an Instron machine. The fracture surfaces of broken specimens were examined in a scanning electron microscope operating at 20 KV.

RESULTS AND DISCUSSIONS

1. As-quenched Alloys

Electron micrographs of as-quenched specimens showed some evidence of decomposition of the matrix in the form of mottled contrast (Fig. 2). Badia, Kirby and Mihalisin³ in studying the strengthening of Cu-Ni-Cr alloys found that precipitation of an almost pure chromium phase took place in the as-quenched specimens. No evidence for this has been found in the present work. Presumably quenching was sufficiently fast to prevent such precipitation.

2. Early Stages of Decomposition

The characteristics of spinodal decomposition as observed in the electron microscope are: (1) satellites in the diffraction pattern; (2) contrast modulations in the image.

When the as-quenched alloys were aged at 700°C and 600°C, a second phase precipitates out from the matrix. Figure 3 shows a (001) diffraction pattern for alloys aged 10 min. at 700°C. The satellites along [100] and [010] on either side of the 200 and 220 spots can be seen in this pattern. These satellites result from a microstructure with periodic composition fluctuations along $\langle 100 \rangle$. These are visible as contrast modulations in bright-field micrographs. For example, Fig. 4 shows these effects in a specimen aged 1 hr. at 700°C.

The wavy appearance of the particles during the early stages of decomposition can be understood qualitatively by considering the changes in microstructure. Livak and Thomas⁵ made an analysis in a Cu-Ni-Fe spinodal alloy and concluded that this wavy appearance is due to the fact that during the early stages of decomposition, the matrix is partially decomposed and the microstructure consists of a multi-dimensional distribution of decomposition products. This distribution changes to a one-dimensional distribution and no preferred (100) habit is developed until the equilibrium tie-lines were reached. Consequently, the microstructure had a wavy appearance as observed in the electron micrographs. The contrast is bright (in bright field) for the Cu-rich phase due partly to preferential thinning.⁵

Cadoret and Delavignette⁶ also studied spinodally decomposed Cu-Ni-Fe alloys and concluded that the contrast results from atomic displacements in the direction of the composition fluctuations or

waves. This is confirmed by the high-resolution electron microscopic studies of the present Cu-Ni-Cr spinodal alloy.⁷ The direction of $\vec{g}$ is normal to the fluctuations which is necessary for this contrast criterion (e.g., Fig. 4). In bright field, bright regions correspond to the larger lattice parameter area characteristic of the Cu-rich phase, while dark regions correspond to the Cu-poor phase.^{2,3}

In spinodally decomposed alloys, the wavelength of the modulations increases with aging time. Hence, as aging continued, the Cu-rich and Cu-poor regions separate into distinct phases and become cuboids. Fig. 5 shows such an example for alloys aged 125 hours at 700°C. The interfaces appear to sharpen, and the wavelength of the periodic structure increases as indicated by the movement of the satellite reflections towards the main spot and eventually become indistinguishable from the matrix spot. This is typical of coarsening e.g., refs. 5, 8.

3. Loss of Coherency

The two phases remain coherent for aging at 700°C for 125 hours (Fig. 5), but loss of coherency is observed after aging 166 hours at that temperature when $\lambda \sim 1000\text{\AA}$. The cuboid-like precipitates join together and some of them start to lose coherency with formation of interfacial dislocation networks⁹ which become prominent after aging for 616 hours at 700°C (Fig. 6), when $\lambda > 1000\text{\AA}$. This behavior is again very similar to that found in Cu-Ni-Fe.¹⁰ Interfacial dislocations are created in order to decrease the strain energy between the two phases.

In Fig. 7, those interfacial dislocations marked D are in contrast when $\vec{g} = [200]$ and $\vec{g} = [11\bar{1}]$, and out of contrast when $\vec{g} = [\bar{1}\bar{1}\bar{1}]$. Hence,

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the Burgers vectors must be either $\vec{b} = \pm a/2 [110]$ or $\vec{b} = \pm a/2 [\bar{1}01]$ which are glissile. This result is again exactly the same as that for Cu-Ni-Fe alloys.^{9,10}

The two phases remain coherent even after aging at 600°C for as long as 808 hours, when the wavelength is $\sim 870\text{\AA}$. Thus it appears that λ must $\geq 1000\text{\AA}$ for the strain energy to be large enough so as to require generation of glide interface dislocations with concurrent loss of coherency.

4. Measurements of Decomposition Wavelength

The wavelength of decomposition can be either measured directly from the enlarged micrographs (large λ) or by calculation from the spacing of satellite spots in the diffraction pattern (small λ), using the Daniel-Lipson equation:¹¹

$$\lambda = \frac{h \tan \theta}{(h^2 + k^2 + l^2) d\theta} a_0$$

where θ = Bragg angle for the (h k l) reflection in a crystal of lattice parameter a_0 , $d\theta$ = angular spacing between a satellite spot and its main reflection.

The measured results are shown in the log-log plot of aging time versus wavelength (Fig. 8). The relation between $\log \lambda$ and $\log t$ is linear in the early stages of decomposition and can be represented by $\lambda \propto t^n$, where n is the slope of the log-log plot. The values of n are 0.25 for 600°C and 0.32 for 700°C. This is very close to the $\lambda \propto t^{1/3}$ law, which is consistent with the theories of diffusion controlled coarsening in which large particles grow at the expense of small ones.^{8,10}

In Fig. 8, the rate of coarsening is linear up to particle sizes $\sim 500\text{\AA}$ corresponding to aging 125 hours at 700°C and 405 hours at 600°C after which the rate appears to accelerate. Since after aging 166 hours at 700°C , interfacial dislocations are observed when $\lambda > 1000\text{\AA}$, but these are not seen after even much longer aging time at 600°C (when the particle size is $< 1000\text{\AA}$), it would appear that coherency is being lost when $\lambda > 500\text{\AA}$. In this case, coarsening can be accelerated as a result of interfacial dislocation motion analogous to creep.¹⁰ If this model is correct, the work hardening rate ($d\sigma/d\varepsilon$) should also increase when interface dislocations are formed due to interactions with slip dislocations. As shown in Fig. 9, there is an increase initially in $d\sigma/d\varepsilon$ upon loss of coherency (curve 3).

5. Mechanical Properties

The results of the tensile tests are shown in Table I, and representative stress-strain curves are shown in Fig. 9. The relationship between yield stress and $\log(\text{aging time})$ is also plotted in Fig. 10. For alloys aged at 700°C , the yield stress remains almost constant between 10 min. and 50 hr. aging time. It then decreases for longer aging times. For alloys aged at 600°C , the yield stress increases with aging time and then levels off to become constant.

The tensile results showed good ductility (Table I) and ductile fracture (dimpled fractographs) when the structure is coherent both after 600°C and 700°C aging. Loss of coherency was observed after long aging times when also discontinuous grain boundary coarsening¹⁷ occurred as was found in Cu-Ni-Fe.^{10,12}

6. Correlations of Microstructure and Mechanical Properties.

The yield stress of the spinodally decomposed alloys increased with aging time corresponding to attainment of the equilibrium tie-line compositions. Dahlgren¹³ has calculated the yield stress of alloys with coherent lamellar microstructures and his theory is based on considering the elastic strains required to maintain coherency between the two phases. The conclusions reached by Dahlgren are that the yield stress of spinodally decomposed Cu-Ni-Fe alloys depends on the difference in cubic lattice parameters of the two phases and is independent of the wavelength and of the volume fractions of the precipitating phases between certain critical values. These conclusions were confirmed by Livak and Thomas.⁵

The physical basis for Dahlgren's calculations was the same as that used by Mott and Nabarro¹⁴ to derive the following expressions for the average internal stress due to spherical, coherent precipitates:

$$\sigma_i \sim 2G\epsilon f$$

where G is the average shear modulus, ϵ is the misfit parameter between solute and solvent atoms, and f is the volume fraction of the precipitating phase.

In Cahn's¹⁵ analysis the yield stress of spinodal alloys should be proportional to the product of the amplitude (A) squared and the wavelength (λ) of the composition modulation, ($A^2\lambda$). However, Ditchek and Schwartz¹⁶ found that this prediction was not consistently observed in Cu-Ti and Cu-Ni-Fe alloys, and so proposed a new mechanism of hardening. In their model, the shear stress due to misfit strains caused by

the passage of a dislocation on its slip plane is calculated. The yield stress increment was thus found to be proportional to $(A/\lambda)S$, where A is the amplitude of the compositional fluctuations, S is a "squaring factor", and when S was substituted by $(\lambda - \lambda_0)$, where λ_0 is the fundamental wavelength of decomposition, a plot of $\Delta Y.S.$ versus $(A/\lambda)(\lambda - \lambda_0)$ showed a linear relationship. Hence, these researchers concluded that S is proportional to $(\lambda - \lambda_0)$. For short aging times, the yield stress increment rises rapidly due to the rapid rise in $(\lambda - \lambda_0)/\lambda$. In the later stages, $(\lambda - \lambda_0)/\lambda$ nears unity and then $\Delta Y.S.$ is proportional to A , which is exactly Dahlgren's argument.

For the present Cu-Ni-Cr alloy, the mechanical behavior is very similar to that of Cu-Ni-Fe alloys. When aged at 700°C, the yield stress does not change much between 10 min. and 50 hr. (Table I). The reason for this may be due to the fact that decomposition has been completed even before 10 min. as suggested from the lattice parameter measurements of this alloy.⁷

The explanation for the decrease in yield stress for still longer aging times may be due to the large wavelength in the microstructure and the fact that the particles begin to lose coherency. The strengthening of the coherent microstructure in decomposed Cu-Ni-Cr alloys arises from the strains associated with the difference in the lattice parameters and also the shear moduli of the two phases. When the particles became semi-coherent, the coherency strains are relieved and thus the yield stress is reduced. The work hardening rate $(d\sigma/d\epsilon)$ then increases (Fig. 9) due to interactions at the interphase interfaces

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between glide and interface dislocations. It was also found, by optical metallography, that discontinuous coarsening, described by Gronsky and Thomas,¹⁷ along grain boundaries occurred, and also results in a decrease of the ultimate tensile stress¹² (Table I).

The yield stress increases as aging time increases for alloys aged at 600°C (Fig. 10). From the above discussion, the correlation between mechanical properties and microstructure does depend on the composition fluctuations. Measurements of Δa using lattice imaging techniques⁷ show that the differences in lattice parameters between the two phases is only ~1% and the experimental errors are too large to ascertain which of the current theories of coherent spinodal hardening is most applicable.

SUMMARY AND CONCLUSIONS

(1) As-quenched specimens showed some sign of decomposition. No pure chromium phase was observed.

(2) The metallography of decomposition in this alloy is almost identical to that of Cu-Ni-Fe alloys when aging at 600°C and 700°C. The microstructure initially consists of fine, wavy particles separated by diffuse interfaces which develop into distinct planar $\{100\}$ interfaces as the wavelength enlarges.

(3) As aging proceeds, coarsening of particles occurs according to the relationships $\lambda \propto t^n$, where $n \sim 1/3$ at 700°C, $n \sim 1/4$ at 600°C.

(4) Loss of coherency is observed for alloys aged at 700°C after 166 hours. Glissile interfacial dislocations with Burgers vector of $a/2 \langle 110 \rangle$ type are created and the coarsening rate is accelerated and the relation between λ and t is no longer linear.

(5) Tensile test results show that the yield stress increases as decomposition takes place until the equilibrium tie-line is reached. A drop in yield stress after aging at 700°C for 166 hours is observed. It is suggested that this is a result of relieving strain when particles begin to lose coherency.

(6) Due to the fact that $(\Delta a)_{\max}$ is very small in this system ($\sim 1\%$), the correlation between mechanical properties and microstructure is not unambiguous. That there is a dependence of the increment of yield stress on Δa can be indicated from the results.

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Table I. Tensile test results of the material at 700°C and 600°C.

(A) 700°C

<u>Aging time</u>	<u>As Quenched</u>	<u>10 min.</u>	<u>1 hr.</u>	<u>50 hr.</u>	<u>166 hr.</u>	<u>616 hr.</u>
Yield stress (KSI)	22.5	41.1	42.3	42.1	36.3	34.6
(MPA)	155.	283.	291.	290.	250.	238.
Ultimate tensile stress (KSI)	51.0	56.8	64.4	61.2	53.2	56.7
(MPA)	352.	391.	444.	422.	367.	391.
Elongation	32%	22%	18%	13%	18%	

(B) 600°C

<u>Aging Time</u>	<u>As Quenched</u>	<u>10 min.</u>	<u>1 hr.</u>	<u>50 hr.</u>	<u>340 hr.</u>	<u>616 hr.</u>
Yield stress (KSI)	22.5	29.6	37.9	48.6	51.4	49.6
(MPA)	155.	204.	261.	335.	354.	342.
Ultimate tensile stress (KSI)	51.0	57.4	58.3	61.1	66.5	65.3
(MPA)	352.	396.	402.	421.	459.	450.
Elongation	32%	25%	16%	8%	8%	7%

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FIGURE CAPTIONS

- Fig. 1. Ni-Cr-Cu ternary phase diagram at 930°C. A: homogeneous b.c.c.; B: homogeneous f.c.c.; C: 2 f.c.c. phases; D: b.c.c. and Cu-rich f.c.c.; E: b.c.c. and Ni-rich f.c.c.; F: b.c.c. and 2 f.c.c. phases.
- Fig. 2. Transmission electron micrograph of as-quenched specimen showing signs of decomposition in the matrix. Foil orientation is (011) and $\vec{g} = [200]$.
- Fig. 3. (001) diffraction pattern of specimen aged at 700°C for 10 min. Satellite spots (S) can be seen along cube directions from 200 and 220 fundamental spots (F).
- Fig. 4. Transmission electron micrograph of alloy aged at 700°C for 1 hour. Foil orientation is (001) and $\vec{g} = [200]$.
- Fig. 5. Transmission electron micrograph of specimen aged at 700°C for 125 hours. Note that the particles are still coherent with the matrix. Foil orientation is (001) and $\vec{g} = [200]$.
- Fig. 6. TEM micrograph of alloy aged at 700°C for 616 hours. Foil orientation is (001) and $\vec{g} = [200]$. At this stage, interfacial dislocations are created and loss of coherency is observed.
- Fig. 7. TEM micrograph of alloy aged at 700°C for 616 hours. Foil orientation is (011) and $\vec{g} = 200$ (in A), $\bar{1}\bar{1}\bar{1}$ (in B), $1\bar{1}\bar{1}$ (in C). Note the interfacial dislocations of type marked D are seen in A and C, but out of contrast in B.

Fig. 8. Plot of $\log(\text{wavelength})$ versus $\log(\text{aging time})$ for alloys aged at 600°C and 700°C .

Fig. 9. Stress-strain curves for alloys aged at 700°C for (1) as-quenched, (2) 10 min., (3) 616 hours, showing work hardening at 2% elongation increasing with aging time, but decreasing slightly later at larger elongations.

Fig. 10. Plot of yield stress versus $\log(\text{aging time})$ for alloys aged at 600°C and 700°C .

-17-

XBL7611-7704

Fig. 1

Fig. 2

XBB-772-810

0 0 0 0 4 7 0 8 0 2 0

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Fig. 3

XBB-760-10143

Fig. 4

XBB 772-815A

0 0 0 0 4 7 0 8 0 2 1

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Fig. 5

XBB 772-813

Fig. 6

XBB-772-812

XBB 760-10647

Fig. 7

XBL7611-7780

Fig. 8

XBL 771-5007

Fig. 9

XBL 7611-7702

Fig. 10

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