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Publication Date
1972-02-01
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February 1972

AEC Contract No. W-7405-eng-48

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MARTENSITIC TRANSFORMATION AND STRENGTHENING OF A SPINODAL Fe/Ni/Cu ALLOY

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ABSTRACT

A 61at.Fe/20at.Ni/19at.Cu alloy has been designed which can be subsequently transformed to martensite following spinodal heat treatment (aging at 850°C). Morphological changes were followed by transmission electron microscopy. Ms temperatures were estimated by an electrical resistivity technique and changes were followed by transmission electron microscopy. Ms temperatures were estimated by an electrical resistivity technique and changes in microhardness were measured. The Ms temperatures increased rapidly, then were unchanged as particle coarsening started and wavelength $\lambda$ increased. The hardness first increased rapidly, then age-softened as $\lambda$ increased.

Although the specimens were brittle, the considerable increases in hardness achieved by martensitic transformation compared to the hardness of purely spinodal alloys indicates that this double phase transformation method may be promising for improving the strength of certain alloys.

1. Now returned to Département Science des Matériaux, Université de Strasbourg, FRANCE.
1. Introduction

Although the spinodal transformation\(^1\) has received increasing attention in recent years (e.g. refs. 2, 3, 4) there have been few reports on the relation between microstructure and mechanical properties apart from recent papers on Cu-Ni-Fe alloys.\(^5,6\)

From a morphological viewpoint, spinodally decomposed alloys appear to be attractive because of the homogeneous character of the microstructure, for example the absence of heterogeneous nucleation on lattice defects and the absence of precipitate-free zones at grain boundaries. Consequently one would predict that good mechanical properties including toughness should be attainable. However, a recent investigation by Livak and Gerberich\(^7\) showed that after spinodal decomposition in Cu-Ni-Fe, specimens fractured intergranularly although the matrices remained ductile. This was attributed to grain boundary segregation, preferential particle coarsening, or a discontinuous precipitation reaction.

Recognizing that the mechanical properties might be limited by these grain boundary reactions it was decided to pursue the idea that in Cu-Ni-Fe alloys it might be possible to choose a composition and aging procedure which on spinodal decomposition would produce an Fe-Ni rich phase which could then be transformed to martensite by quenching. In other words it might be possible to produce martensite in a "dispersion" of the second phase (copper rich) resulting in an alloy of improved tensile strength. This concept is similar to the idea of dispersion strengthening martensite utilizing ausaging techniques and the more familiar ausforming method.\(^8\)
2. Design of the Alloy

The work of Köster and Dannöhl\(^9\) on the Fe-Ni-Cu phase diagram allows an estimation to be made of the range of composition of alloys which can be both spinodally and martensitically transformed. Figure 1 shows the Fe-Ni-Cu ternary system with the miscibility gap indicated by Curve I. Curve II shows the solvus isotherm at 600°C. We have also indicated the positions of four tie-lines at 600°C (dotted lines a, b, c and d). 600°C is chosen as a reasonable lower limit of temperature for suitable aging kinetics. The compositional range between Curve I and the Fe-Cu axis is not suitable for this investigation since it is not a single phase field.

The influence of copper on the martensitic transformation of Fe-Ni alloys is little known. However, a close inspection of the phase diagrams of the two binary systems Fe-Cu and Fe-Ni suggests that copper and nickel have similar influences on the Ms temperature of Fe. Therefore, for a martensitic transformation to occur in a single phase ternary alloy it was estimated that to a first approximation, the total of (Cu+Ni) must be lower than 35 wt%. In a multiphase alloy this condition applies to the iron-rich phase. From Figure 1 it can be seen that a fully decomposed alloy having a composition along the tie-line d satisfies the above condition at 600°C. All alloys situated in the compositional range between the tie-line d and the Fe-Cu axis, therefore, are predicted to transform martensitically.

The second requirement that the alloy must satisfy, i.e. that it decomposes spinodally, is obtainable only between Curves I and II (Fig. 1). According to Butler and Thomas,\(^5\) in the Cu-Ni-Fe system, where coherency stresses are low, an alloy inside the spinodal has a volume fraction of one or other of the two phases of at least approximately 20%. Butler\(^10\)
further confirmed that the effect of coherency strains on the position of the spinodal is small in Cu-Ni-Fe alloys (see Fig. 1, ref. 5) hence it is concluded that the single phase alloy required for this investigation must be as close as possible to Curve I.

The compositional range shaded in Figure I satisfies the two conditions discussed above and so an alloy containing 20 at% Ni and 19 at% Cu was made up. The aging characteristics were studied morphologically and specimens were also quenched in order to obtain the martensitic transformation. Unfortunately it was not possible to perform tensile mechanical tests because of the extreme brittleness of the alloy, but microhardness was used to demonstrate the changes in properties that occurred.

3. Experimental Procedures

3.1 Materials and heat treatment

The alloy was prepared by vacuum melting 99.999% Cu, 99.85% Ni and 99.6% Fe followed by chill casting into copper molds to minimize segregation. The composition in at% found by chemical analysis was: 61% at Fe, 20% at Ni, 19% at Cu. After homogenization of the ingot, the solvus temperature was determined experimentally to be 1125°C (+ 25°C). The spinodal temperature is estimated from Ref. 9 to be greater than 850°C so this temperature was chosen for aging.

Slices were cut from the ingot, solution treated at 1150°C for 40 min. in evacuated quartz tubes and then quenched by breaking the tubes under water. Groups of specimens were aged at 850°C for 3 min, 9 min, 2 hrs. and 20 hrs. For aging times of 3 and 9 min, a salt bath was used. After this treatment, specimens were water quenched and some subsequently quenched in liquid nitrogen to produce martensite.

3.2 Electron microscopy

The slices cut from the ingot could not be rolled due to pre-existing cracks in the ingot. They were thinned by chemical polishing (20 ml
acetic acid, 10 ml nitric acid and 4 ml hydrochloric acid). Final electropolishing was conducted in a jet-polishing apparatus using a chromic-acetic acid solution (75g CrO₃, 400 ml HAC and 25 ml H₂O). Some preferential polishing of one of the two phases always occurred. Foils were examined in a Siemens Elmiskop IA operated at 100 kV or in a Hitachi operated at 650 kV.

3.3 Measurement of $M_s$ temperatures

The $M_s$ temperatures of the alloy were estimated using an electrical resistivity technique. The sample in the form of a small strip (approximate dimensions 3/4" x 1/8" x 1/50") was slowly lowered into a tall vertical double-walled glass cylinder in which a temperature gradient from room temperature to -196°C was maintained by having liquid nitrogen at the bottom. Enough time was allowed for the specimen to reach thermal equilibrium at each step. The voltage required to pass a constant current in the sample was recorded. The temperature was measured at the same time using a thermocouple placed midway along the length of the sample. The voltage-reading, which was proportional to the resistivity, was plotted against the temperature and $M_s$ was estimated as the temperature at which a sharp drop in resistivity occurred. The accuracy of the measurement was about ± 10°C.

3.4 Mechanical properties

The only mechanical property that could be determined was the microhardness since the alloy was brittle and the original ingots contained many cracks produced during the quench.

Vickers microhardness values were determined using a Seitz Wetzlar microhardness testing unit with an applied load of 500 g on a sample.
0.020" thick. At least 10 measurements were made on each specimen and the hardness values reported for each specimen are average values.

4. Experimental Results

4.1 Microstructure of the spinodally decomposed alloys

4.1.1 Morphology

The microstructure of the as-quenched and aged alloys are shown in the transmission electron micrographs of Fig. 2. The micrograph in Fig. 2a shows a periodic modulation of the order of 150Å in the as-quenched alloy, indicating that spinodal decomposition occurred during the quench. The changes in microstructure with aging time represented by Figs. 2b, c and d, show similar features to those observed by Butler and Thomas\(^5\) and Livak and Thomas\(^6\). For the small-wavelength samples, \(\lambda < 250\)Å, the microstructure consists of wavy plates lying primarily along (100) planes which is typical of non-symmetrical spinodal alloys. In the larger wavelength samples coherent interfaces parallel to (100) planes have developed between the Cu-rich and the Fe-Ni rich phases. The difference in lattice parameters between the two phases is -0.4% once coarsening has started.

The contrast which allows the two phases to be distinguished results mainly from the difference in thickness between the Cu-rich and the Fe-Ni rich phases. Butler and Thomas showed that the Cu-rich phase is preferentially thinned during electro-polishing, and in the present alloy this problem was such that holes could not be prevented from forming at the Cu-rich phase in the thinnest areas.

4.1.2 Measurement of wavelength

Characteristic sidebands of spinodal decompositions were
not observed in low order reflections in the diffraction patterns. This agrees with Butler and Thomas who found that sidebands in Fe-Ni-Cu alloys are only detected in spot patterns from alloys with a wavelength smaller than about 150Å, and in the present case such a wavelength was already present after quenching. Consequently the measurements of wavelengths were done from enlarged prints: the results are shown in Table I.

TABLE I

<table>
<thead>
<tr>
<th>time of aging at 850°C</th>
<th>wavelength in Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>150</td>
</tr>
<tr>
<td>3'</td>
<td>205</td>
</tr>
<tr>
<td>9'</td>
<td>360</td>
</tr>
<tr>
<td>120'</td>
<td>890</td>
</tr>
<tr>
<td>1200'</td>
<td>1930</td>
</tr>
</tbody>
</table>

Except for the first few minutes the variation of wavelength with aging time could best be expressed by a \((\text{time})^{1/3}\) relationship (Fig. 3), in good agreement with previous data.5,6

4.2 Ms temperatures

Preliminary diffractometer experiments conducted on bulk samples showed that the Ms temperatures were always between room temperature and -196°C regardless of the wavelength.

Typical resistivity results are shown in Fig. 4. Curves a and b show the variation of resistivity with temperature for the alloys as-quenched and aged 20 hrs. at 850°C respectively. The variation of Ms temperature with aging time is shown in Fig. 3. After short aging, Ms has increased from -137°C to -50°C and remains constant after further aging.
However, it was observed by electron microscopy that foils prepared from aged alloys were always partially transformed to martensite. The percentage of martensite increased when the thickness decreased and when the wave-length increased. For example, thinning by electropolishing of the aged alloys causes the apparent Ms temperature of these alloys to be increased from -50°C to above 0°C.

4.3 Microstructure of martensite

The micrographs in Figs. 5 and 6 show the structure of the martensite, viz., after quenching the as-quenched alloy (Fig. 5) and the 20 hrs. aged alloy (Fig. 6a,b) into liquid nitrogen. These alloys were observed in the high voltage electron microscope at 650 kV. In the as-quenched alloy martensite exhibits plate-like morphology with well-defined interfaces (Fig. 5). These plates are mostly twinned but twinned and dislocated areas are often observed. This is similar to martensite in Fe-Ni alloys (e.g. ref. 11). On aging the morphology changes until in the 20 hrs.-aged alloy, the martensite has only a few well-defined interfaces (Fig. 6). The size of the martensite plates exceeds the wavelength of the spinodal and the martensite substructure is a mixture of twins and dislocations.

4.4 Hardness results

The experimental results are summarized in Fig. 7. The microhardness of the water-quenched alloys is nearly constant until the wavelength reaches 900A after which it decreases slightly.

For alloys quenched in liquid nitrogen the microhardness is much higher. It rapidly increases after short aging and continuously decreases after 3 minutes. This result is similar to the age-hardening behavior of dispersion strengthened alloys.
5. Discussion

5.1 Morphology and kinetics

The morphology of the spinodal decomposition reaction (Fig. 2) and kinetics of growth (Fig. 3) are very similar to those obtained on the asymmetric spinodal alloys studied by Livak and Thomas. There is a two-step aging process. Initially the diffuse wavy morphology is associated with no wavelength change, presumably whilst the alloy composition approaches equilibrium given by the tie-line. This can be inferred from the variation of Ms temperature (Fig. 3) which can be assumed to depend linearly with composition. In the second stage, coarsening then proceeds at constant composition with large particles growing at the expense of smaller ones, i.e. classical Ostwald ripening as discussed in earlier papers. Thus, the Ms temperature does not appear to be affected by the interparticle distance \( \lambda \), but only by composition.

Wavelength does, however, have an influence on the subsequent martensite morphology. The interfaces become more diffuse as \( \lambda \) increases and the tendency for twinned substructures is reduced. In all cases the martensite plates are much larger than the interparticle spacings (Figs. 5,6).

As is now well known, martensite transformations can occur spontaneously during specimen preparation for electron microscopy. For example, Warlimont found an increase in Ms as specimen thickness was reduced. We found exactly the same behavior, e.g. bulk samples with Ms at -50°C transformed to martensite at room temperature when thinned to foils. However, in the present work the thinning dissolves preferentially the copper-rich phase and it is likely that the martensite transformation is then triggered by strain release due to this preferential dissolution.
This result is similar to that obtained by Kinsman on Cu-Fe alloys\textsuperscript{13}.

5.2 Mechanical properties

The influence of the martensitic transformation on the microhardness of the alloy for the different heat treatments is substantial, particularly when compared to the hardness of other purely spinodal Cu-Ni-Fe alloys (Fig. 7). The explanation for the "age-hardening" behavior, i.e. the change in hardness associated with martensite formed in specimens containing varying wavelengths is not simple. The amount of martensite formed in alloys previously aged and then quenched is much higher than that in the as-quenched alloy because of the higher value of $M_s$ in the former case. This probably accounts for the large increase in microhardness observed between the alloys as-quenched and aged 3 min. at $850^\circ C$ (Fig. 7). The subsequent decrease in hardness associated with coarsening of the spinodal is related to the increase in interparticle spacing and diffuseness of the martensite - martensite interfaces. Although the composition of the martensite seems to be constant when softening occurs there may also be an effect associated with the substructural changes, viz. the decrease in internal twinning. However, the important result and the one that was sought, is the considerable gain in strength that is possible by martensitically transforming spinodal alloys. Further investigations of this phenomenon and attempts to obtain more ductile alloys so that tensile properties can be measured are under way.

6. Summary

The influence of aging treatments on the kinetics and morphology of the decomposition observed in the studies alloy is very similar to those observed by Livak and Thomas in spinodally decomposed alloys. Thus, we believe that in the alloy designed, viz. 19Cu/20Ni/61 Fe, spinodal
decomposition also occurs and therefore it can be concluded that martensitic transformations can occur in spinodally decomposed Cu/Ni/Fe. This effect has also been found in spinodal Cu-Mn-Al alloys.¹

The spinodal decomposition influences the martensitic transformation by two different ways: by the changes of composition itself and by the periodicity of the composition. It is possible to separate these two influences because the periodicity begins to be modified only when no further change in composition occurs. The changes of composition produce a large increase in Ms temperature. By comparison the influence of the wavelength is less spectacular and is limited to some modifications of the martensite substructure.

The values of the microhardness are not much modified by the spinodal decomposition itself. On the other hand subsequent transformation to martensite produces large increases in hardness. The greatest hardness was obtained when particle coarsening was just occurring, beyond which softening occurred, but even after prior aging for 20 hrs. the hardness had still not decreased to that of the as-quenched value.

Acknowledgements

This work was done under the auspices of the U.S. Atomic Energy Commission through the Lawrence Berkeley Laboratory, University of California, Berkeley. One of the authors (C. Vercaemer) expresses his gratitude to the North Atlantic Treaty Organization and to the Centre National de la Recherche Scientifique for their financial support.
Figure Captions

Fig. 1. Fe-Ni-Cu ternary system according to W. Köster and W. Dannöhl (ref. 9). Curve I represents the miscibility gap at temperatures near the solidification temperature (~1095°C at the iron-rich end and 1220°C at the maximum) and Curve II is a solvus isotherm at 600°C respectively. Lines a, b, c and d are tie-lines at 600°C. The alloy used in this study is represented by + (59wt% Fe, 20wt% Ni, 21wt% Cu).

Fig. 2. Transmission electron micrographs in bright field.
(a) as quenched: \( \lambda = 150\AA \), and aged at 850°C for (b) 3 min, \( \lambda = 205\AA \), (c) 9 min, \( \lambda = 360\AA \), (d) 2 hrs, \( \lambda = 890\AA \).

Fig. 3. Variation of wavelength and Ms temperature with \((\text{aging time})^{1/3}\).

Fig. 4. Typical curves obtained during the measurement of Ms temperature by the electrical resistivity technique.

Fig. 5. Transmission electron micrograph showing martensite (M) in the as quenched alloy.

Fig. 6. Transmission electron micrographs showing martensite in the 20 hr. aged alloy; (a) bright field, (b) dark field of austenite spot reversing contrast. M represents the martensitic area and A the austenitic area.

Fig. 7. Variation of hardness with aging time for samples quenched in water and in liquid nitrogen. Aging temperature 850°C. Livak and Thomas' results (ref. 6) have been represented for comparison (aged at 625°C compared to 850°C in the present alloy).
References

Fig. 1
Fig. 2
Fig. 3
Fig. 4

+ sample as-quenched
○ sample aged 20 hrs. at 850 °C

V ~ resistivity

T °C
Fig. 7

Microhardness HV

+ quenched in water
x quenched in liquid nitrogen
○ Livak and Thomas
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