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AN UNUSUAL CS-CL STRUCTURE FOR GOLD-COPPER IN G.P. ZONES FORMED IN ALPHA IRON-GOLD-COPPER

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Publication Date

1966-08-01

UCRL-17052

University of California
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Submitted to Acta Metallurgica

UCRL-17052

UNIVERSITY OF CALIFORNIA

Lawrence Radiation Laboratory
Berkeley, California

AEC Contract No. W-7405-eng-48

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August, 1966

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ABSTRACT

Alpha iron was supersaturated with equal atomic amounts of gold and copper by quenching a gamma Fe-Au-Cu solid solution. G.P. zones with the Cs-Cl structure were produced by low temperature aging. The kinetics of formation of the ordered structure follow the pattern characteristic of spinodal decomposition.

I. INTRODUCTION

A. Binary Iron-Gold and Iron-Copper Alloys

Gamma iron can dissolve up to 8.1 atomic percent of gold⁽¹⁾ or about the same amount of copper.⁽²⁾ The $\gamma \rightarrow \alpha$ phase transformation occurs on quenching when either of these elements is in solution, just as it does in pure iron.^(1,3) Neither of these elements is highly soluble in alpha iron^(1,2), thus BCC iron can be highly supersaturated with either gold or iron by quenching solution treated alloys from high temperatures.

These supersaturated alloys age harden.⁽⁴⁻⁶⁾ Gold has been shown to form G.P. zones in BCC iron⁽⁵⁾ under some conditions even though the gold atomic radius is 13% larger than that of iron. However, gold also precipitates discontinuously on lattice imperfections.⁽⁷⁾ Copper atoms, on the other hand, are only about 1% larger than iron, and copper precipitates rapidly as fine FCC particles.⁽⁶⁾ The difference in behavior can be attributed to the gold atom, which is much larger than iron, thus high stresses are generated in the lattice when a gold precipitate nucleates.

B. Binary Gold-Copper Alloys

Several ordered structures form in Au-Cu alloys, but none has the Cs-Cl (B2) structure.⁽⁸⁾ The B2 structure is the simplest that an ordered AB type alloy can form and it is stable for many 50 at. % A-B intermediate phases even when the component elements crystallize in the FCC structure. For example, an alloy of Cu-40 at. % Pd forms the B2 structure below 600°C, although the Cu-Pd phase diagram is quite similar to that of Au-Cu. Both the heat of mixing

$$(\Delta H_{\max} = 2600 \frac{\text{cal}}{\text{gm atom}} \text{ for Cu-Pd}^{(10)} \text{ and } \Delta H_{\max} = 1300 \frac{\text{cal}}{\text{gm atom}} \text{ for Au-Cu}^{(11)})$$

and the atom radius ratio

$$\left(\frac{r_{\text{Pd}}}{r_{\text{Cu}}} = 1.08 \text{ and } \frac{r_{\text{Au}}}{r_{\text{Cu}}} = 1.13 \right)$$

are more favorable for the formation of the B2 structure in Cu-Pd. Nevertheless, Au-Cu can assume the B2 structure when co-precipitation occurs in a BCC environment. This structural configuration probably has an energy near to the energies of the structures normally found in Au-50 at. % Cu alloys.

C. Objectives of This Investigation

Because no intermediate phases are formed in Au-Fe⁽¹⁾ or Cu-Fe⁽²⁾ alloys, it is reasonable to expect that precipitates separating from BCC iron alloys that are supersaturated with respect to both gold and copper, will contain iron only in solid solution. A fair degree of control can thus be maintained over the properties of the precipitate. For example, the average atomic radius of the precipitate can be varied from that of copper to that of gold by controlling the ratio of gold to copper atoms in the alloy. The average atomic radius of the precipitate in an alloy with equal atomic percentages of gold and copper will be approximately 7.5% larger than the radius of iron. Thus coherent precipitates forming in such an alloy will produce much less strain energy than gold G.P. zones forming in binary Fe-Au alloys. A greater tendency for the formation of G.P. zones and a lesser tendency for discontinuous precipitation on imperfections is to be expected for the Fe-Au-Cu alloys (when compared with binary Fe-Au alloys).

With gold and copper present in equal atomic percentages in supersaturated alpha Fe-Au-Cu, it seemed likely that the precipitate forming at low temperatures would be forced to take the B2 structure because of

the similarity of the B2 and BCC structures, and because of the acceptable ratio of gold to copper atom sizes for the B2 structure.

In view of the above considerations, the following experiments were conducted on an iron alloy containing equal atomic percentages of gold and copper:

1. The supersaturated BCC alloy was aged at low temperatures and examined to determine whether or not G.P. zones had formed.
2. The aged alloy was examined to ascertain whether or not the Au-Cu precipitate was ordered.
3. The kinetics of the age hardening process were followed and compared with the results from similar experiments on binary Fe-Au and Fe-Cu alloys.

II. EXPERIMENTAL PROCEDURE

Samples of an iron alloy containing 3.8 at % each of gold and copper were homogenized in evacuated quartz capsules at either 950°C or 1125°C. The samples were quenched from their homogenization temperatures by breaking the capsules under water. All quenched samples were found to be two phase. From lattice parameter measurements the iron-rich grains were estimated to contain 1.1 at. % each of gold and copper when quenched from 950°C, and 2.6 at. % each when quenched from 1125°C. Lattice parameters were determined by extrapolation of data taken from Debye-Scherrer powder patterns. The camera radius was 5.73 cm and FeK α radiation was used. The iron rich grains which were quenched from 950°C and 1125°C had lattice parameters of 2.879Å and 2.891Å, respectively. The aging of the quenched samples was carried out at 400°C and 350°C in evacuated quartz capsules. The kinetics of decomposition in the supersaturated iron-rich grains were followed with microhardness measurements. Ten microhardness impressions were made with a

300 gm load in the iron rich grains, and the readings were averaged for each microhardness data point.

III. RESULTS

Figure 1 shows the selected area diffraction pattern from a sample quenched from 950°C and aged 8 hours at 400°C plus three days at 350°C; it is clearly of the BCC type. The electron beam was nearly parallel to [001]. The streaked pattern shows that plate-like zones had formed on the {100} planes of the matrix because these streaks are parallel to all <100> directions. The streak asymmetry indicates that the size of the body-centered cell in the zone is slightly larger than that of the iron matrix. Also apparent are the intensity maxima at 100 spot positions. These spots are not characteristic of the BCC lattice but indicate the presence of a Cs-Cl type superstructure for the Au-Cu zones. Intensity maxima can be obtained from BCC structures at 100 positions if the foil specimen is extremely thin. The foil used for the diffraction pattern in Fig. 1 was relatively thick however, and it is highly unlikely that the 100 spots are due to thin foil effects. The streaked appearance of the 100 spots also supports the conclusion that these are superlattice spots from the ordered G.P. zones.

Streaks and superlattice spots were also observed in a pattern from a sample aged 8 hours at 400°C, but the superlattice spots were not quite as clearly defined as those shown in Fig. 1. The appearance and size of the zones observed in transmission microscopy for the Fe-Au-Cu alloy were the same as observed in a similarly treated Fe-Au alloy.⁽⁵⁾ Figure 2 gives the age hardening response of samples quenched from 950°C and 1125°C and aged at 400°C.

IV. DISCUSSION OF RESULTS

It is evident that the sum of the atomic percentages estimated for gold and copper in solution in gamma iron is much less than the solubility of either element alone. This is not entirely unexpected because the average positive heat of solution of gold and copper in iron is effectively raised in magnitude by the negative heat of mixing of copper in gold when a Au-Cu alloy is dissolved in iron.

The increased positive heat of solution, however, aids the decomposition of the supersaturated BCC iron. Both microhardness curves, Fig. 2, show an extremely rapid increase for very short aging times. This is in contrast with the sigmoidal hardening curves of an Fe-3.8 at. % Au alloy and an Fe-1.23 % Cu alloy, which show hardness peaks after 20 hours at 400°C (Fe-Au), and 8 hours at 500°C (Fe-Cu). These latter alloys however, were not saturated with solute at the solution treating temperatures, whereas the samples used in the present study were saturated, and this could account for the differences in decomposition behavior. The hardening response shown in Fig. 2 is similar to that produced by spinodal decomposition in that there is no evidence of the incubation period required for a nucleation process. The maximum hardness of the sample with the lower solute content (472 DPH, curve a, Fig. 2) is lower than the maximum hardness of the sample with the higher solute content (625 DPH, curve b, Fig. 2), and it is reached after a longer aging time (8 hours vs. 1 hour), even though the general shapes of the two curves are the same.

The maximum hardness of the sample quenched from 1125°C is very high. G.P. zone formation undoubtedly accounts for most of the increased hardness, but the interaction of dislocations with ordered structures in precipitates can also account for yield stress and hardness increases. (12,13)

V. CONCLUSIONS

1. G.P. zones similar to those found in Fe-Au alloys were found in an alloy of Fe-Au-Cu.
2. The G.P. zones possessed the Cs-Cl (B2) structure.
3. The age hardening response was similar to that produced by spinodal decomposition.

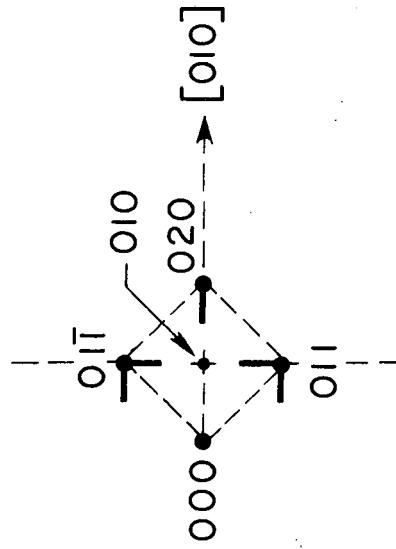
ACKNOWLEDGMENTS

The author wishes to thank Professor E. R. Parker for his helpful discussion of this work. This work was financially supported by the United States Atomic Energy Commission.

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FIGURE CAPTIONS

- Fig. 1. Electron diffraction pattern from the iron-rich grains of a sample of iron-gold-copper quenched from 950°C, and aged 8 hours at 400°C plus 3 days at 350°C.
- Fig. 2. Microhardness of the iron rich grains vs. aging time at 400°C for, a) a sample of iron-gold-copper quenched from 950°C, and b) a sample quenched from 1125°C.



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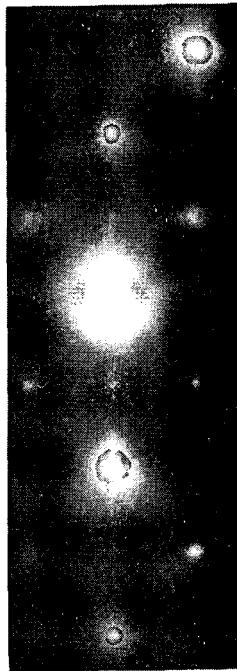
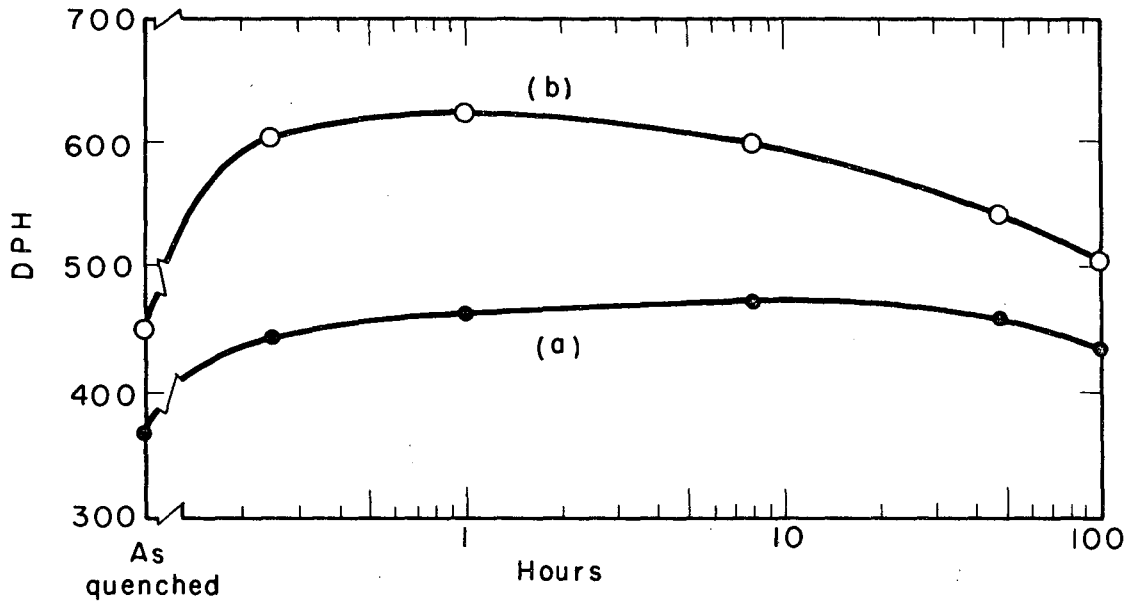


Fig. 1



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Fig. 2

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