Communications

Decomposition of Rapidly Solidified Cu-Ti Solid Solutions

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The decomposition process in copper rich Cu-Ti alloys has been studied by a number of investigators.[1-7] The process is a complicated one, involving short range order (SRO), spinodal decomposition, and long range ordering (LRO). The sequence of these processes has been a matter of some question. Laughlin and Cahn,[2,3] on the basis of electron microscopy studies of alloys quenched from the solid solution region, reported that spinodal decomposition preceded LRO. This was based on the greater intensity of the satellite reflections relative to the LRO reflections in a $Cu_{95}Ti_5$ alloy. Furthermore, a $Cu_{97}Ti_3$ alloy was observed to decompose without any apparent formation of LRO. Biehl and Wagner,[6,7] however, reported that long range ordering always occurred concomitantly with decomposition. This was based on a careful atom probe field ion microscopy investigation. They never observed decomposition without simultaneous ordering.

In the discussions to date, no mention has been made of the importance of the SRO that exists in the metastable solid solution. Recently, Ino[8] and Laughlin, Lee, and Alexander[9] have investigated the ordering process in bcc based structures in zeroth approximation, using first and second neighbor interactions. In conformity with the earlier works of Adachi[10] and Richards,[11] they found that a solid solution must order first *before* it can decompose into two phases. This has been found experimentally in the work of Allen and Cahn on Fe-Al alloys.[13,14]

The purpose of the present investigation was to use the technique of rapid solidification to study the three above-mentioned reactions in a Cu-Ti alloy and to ascertain which one of the reactions precedes the others.

An alloy of composition corresponding to $Cu_{85}Ti_{15}$ was prepared by arc melting 99.99 pct pure copper and 99.98 pct pure titanium in a helium atmosphere. Ten-gram buttons were prepared and melted four times to ensure a completely homogeneous alloy. A conventional copper wheel of 7.8 cm outer diameter was used for melt-spinning ribbons of the alloy under vacuum. In each case, approximately 3 gms of the alloy were induction-melted in a silica tube having an orifice diameter of 0.8 mm, and ejected with a 16 psi back-pressure of helium gas. The thickness of the resulting ribbons ranged between 40 and 50 microns. The maximum cooling rate was estimated to be about 5×10^5 K per second for a wheel speed between 8000 and 8100 rpm. This estimate is based on the experimental observations and theoretical modeling of cooling rates by Ruhl[12] for the case of splat quenching. The parameters that Ruhl found to be of greatest importance in determining the cooling rate were the splat thickness and the interface heat transfer coefficient.

Samples of a metastable $Cu_{85}Ti_{15}$ ribbon were subjected to the following heat treatments: 300 °C/100 minutes and 398 °C/1140 minutes. In each case, pieces of the as-quenched ribbon were evacuated in pyrex ampules back-filled with 0.5 atm of helium. The temperature of the furnace was regulated to within plus or minus 1 °C. After heat treatment the ampules were quenched in an ice brine solution supercooled to a temperature of -10 °C, thus causing the pyrex ampules to crack, and ensuring a rapid quench.

The as-quenched ribbons were characterized initially using X-ray diffraction. A Rigaku X-ray diffractometer with a Cu$K\alpha$ source was used. Both the heat treated and the as-quenched ribbons were characterized using a JEOL 100 CX Transmission Electron Microscope (TEM). A dual gun Gatan Ion Miller Model 6000 was used to thin the ribbons for TEM observation using a gun current of 1 mA and a gun voltage of 6 kV.

The results of Laughlin and Cahn[2,3] are summarized in Figure 1. This schematic shows that an as-quenched $Cu_{95}Ti_5$ alloy has SRO (the $\{1\frac{1}{2}0\}$ reflections), spinodal decomposition (satellites), and LRO ($D1_a$ reflections). With aging, the $\{1\frac{1}{2}0\}$ reflections decreased in intensity and the intensity of the $D1_a$ reflections increased.

An electron diffraction pattern of a $Cu_{85}Ti_{15}$ alloy that has been rapidly quenched from the liquid is shown in Figure 2. The existence of $\{1\frac{1}{2}0\}$ SRO reflections is evident, but the LRO, $D1_a$ reflections are absent. At the same time oxide reflections can be seen near some fundamental reflections. Diffraction patterns were also obtained with a highly defocused condenser lens, and no satellites were observable. Thus, the as-quenched state of the $Cu_{85}Ti_{15}$ alloy involves only the SRO.

When the as-quenched alloys were heat treated at the temperatures and times given in the experimental procedure

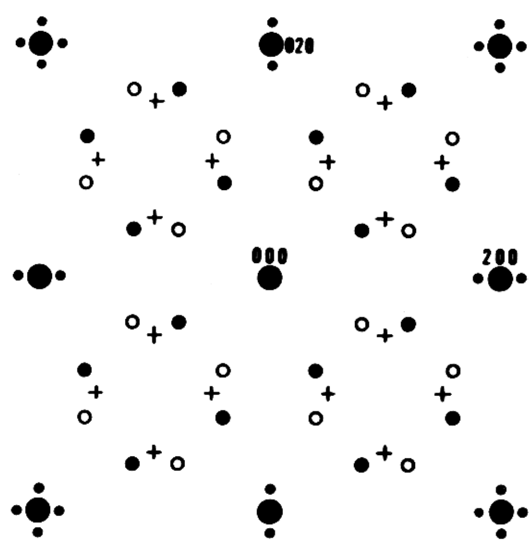

Fig. 1 — Schematic of a [001] diffraction pattern of an as-quenched $Cu_{95}Ti_5$ alloy. The satellites represent long wavelength modulations, the crosses represent SRO, and the dots represent two variants of the LRO phase.

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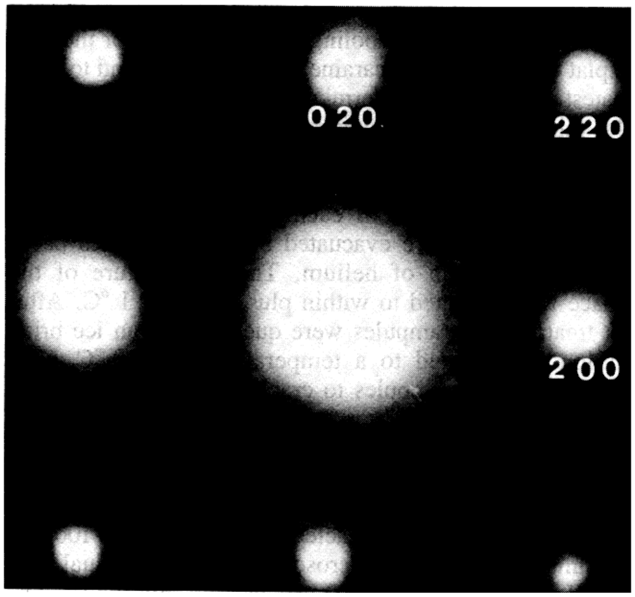

Fig. 2 — A [001] diffraction pattern of an as-quenched $Cu_{85}Ti_{15}$ alloy. Note that the SRO reflections are present and some oxide reflections. No LRO reflections are observed.

section, the $D1_a$ reflections appeared. Thus, the $Cu_{85}Ti_{15}$ alloy orders before the spinodal decomposition process begins, in a similar way as the Fe-Al alloy and as the solid solution models predict. In the present case, however, the ordering process that occurs *prior* to the decomposition is different from the ordering process which occurs concomitant with it. Using the terminology of de Fontaine[15] the later process can be called "spinodal ordering." Accepting Biehl and Wagner's interpretation of the LRO reaction and spinodal decomposition we have the following sequence of reactions in Cu-Ti alloys:

$$\alpha \rightarrow \alpha'(\mathrm{SRO}) \qquad \text{Reaction [1]}$$

$$\alpha'(\mathrm{SRO}) \rightarrow \alpha + \mathrm{D1_a} \qquad \text{Reaction [2]}$$

where α' (SRO) is the short range order state, α is the disordered fcc Cu alloy, and $D1_a$ is the LRO ordered Ti-enriched phase. Reaction [1] is the spinodal ordering reaction; Reaction [2] is the concomitant decomposition and LRO reaction reported and described by Biehl and Wagner.[7,8]

In summary, we have demonstrated that a supersaturated Cu-Ti solid solution decomposes *after* the spinodal ordering reaction. We were able to do this because of the high rate of quenching made possible by the melt spinning technique. The decomposition process in Cu-Ti is thus similar to other binary alloys that both order and decompose. Furthermore, the Cu-Ti alloy is similar to the Ni-Mo alloy in which a $\{1\frac{1}{2}0\}$ SRO solid solution is also obtained prior to the formation of the LRO $D1_a$ phase.[16]

REFERENCES

1. J. A. Cornie, A. Datta, and W. A. Soffa: *Metall. Trans.*, 1973, vol. 4, p. 727.
2. D. E. Laughlin and J. W. Cahn: *Metall. Trans.*, 1974, vol. 5, p. 972.
3. D. E. Laughlin and J. W. Cahn: *Acta Metall.*, 1975, vol. 23, p. 329.
4. A. Datta and W. A. Soffa: *Acta Metall.*, 1976, vol. 24, p. 987.
5. T. Hakkarainen: Doctor of Technology Thesis, Helsinki University of Technology, Ontaniemi, Finland, 1971.
6. K. E. Biehl and R. Wagner: *Proc. 27th Int. Field Emission Symp.*, Tokyo, 1980, p. 267.
7. K. E. Biehl and R. Wagner: *Proceeding of An International Conference on Solid-Solid Phase Transformations*, Pittsburgh, PA, AIME, Warrendale, PA, 1981, p. 185.
8. H. Ino: *Acta Metall.*, 1978, vol. 26, p. 827.
9. D. E. Laughlin, K. B. Alexander, and L. L. Lee: *Proceedings of 2nd Acta/Scripta Metallurgica Conf.*, P. Haasen, V. Gerold, R. Wagner, and M. F. Ashby, eds., Pergamon Press, Oxford, 1984, pp. 221-26.
10. K. Adachi: *Sci. Rep.*, Tohoku Univ., Ser. 1, 1951, vol. 15, p. 30.
11. M. J. Richards: Sc.D. Thesis, M.I.T., Cambridge, MA, 1971.
12. R. C. Ruhl: *Mat. Sc. Eng.*, 1967, vol. 1, p. 313.
13. S. M. Allen and J. W. Cahn: *Acta Metall.*, 1975, vol. 23, p. 1017.
14. S. M. Allen and J. W. Cahn: *Acta Metall.*, 1976, vol. 24, p. 425.
15. D. de Fontaine: *Acta Metall.*, 1975, vol. 23, p. 553.
16. L. A. Nesbit and D. E. Laughlin: *Acta Metall.*, 1978, vol. 26, p. 815.

A Novel Solidification Technique of Metals and Alloys: Under the Influence of Applied Potential

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A technique has been devised by which liquid alloys are cooled under direct electrical potential to bring changes in the normal process of nucleation and growth of equilibrium phases. Earlier Vashchenko *et al.*[1] have used electric current (d.c.) through the sand mold (one electrode was the mold frame and the other was the casting itself) to effect changes in the as-cast structures of cast irons. However, the effect of the hydrogen concentration change[1] in the melt due to the hydrogen evolution by the passage of current in the moist mold could not be ruled out. The present experiments were carried out with low melting Pb-15 pct Sb-7 pct Sn (monotype metal) alloy in glass tubes of 5 mm diameter and 100 mm long with electrodes on both ends of the tube in direct contact with the melt. Thus, the applied potential is entirely responsible for the observed modification of the structure.

The glass tube assembly with the alloy in it was melted in a vertical resistance furnace, heated to a temperature about 50° above the melting point, and then furnace cooled (with the natural furnace cooling rate of few degrees a minute) while direct current (30 to 40 mA/cm^2 at about 30 V) was passed through the melt until the completion of solidification. In the same furnace, another sample was also solidified under exactly the same conditions with no applied potential.

Figure 1 shows the as-cast microstructure of the Pb-Sb-Sn alloy when solidified from liquid state without the applied potential. Figures 2(a) and (b) indicate the modified microstructure at low and high magnifications of the same alloy when solidified under an applied electrical potential.

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