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NSF-tr-58
August, 1953

Applied Physics Translated from Doklady Akademii Nauk SSSR, 89, 669-72 (1953)

On the Effect of Certain Dissolved Admixtures on the Frontal Diffusion of Silver into Polycrystalline Copper

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It has been found that small amounts (small relative to the solubility at the given temperature) of antimony and beryllium in solid solution in copper substantially affect the rate of diffusion of silver into copper and the shape of the diffusion front.[1] It was found that an increase in the antimony content in a copper-antimony solid solution accelerates the diffusion of silver into this solid solution. Because of this, when the average concentration of antimony is small in the polycrystalline solid solution, irregularities of the diffusion front appear clearly wherever the concentration of antimony is highly nonuniform. Along the intercrystalline boundaries, where the concentration of antimony is considerably increased because of internal adsorption,[2] the diffusion of silver proceeds much faster than within the grains themselves, and the diffusion front penetrates the copper in wedges along the grain boundaries.

Beryllium, like antimony, enriches the layers adjoining the grain boundaries of polycrystalline copper; but, unlike antimony, it retards the diffusion of silver into the copper-beryllium solid solution. (This fact, however, cannot cause a local retardation of the diffusion front near the grain boundaries, since the diffusion reaches such "lagging" sectors from the side, i. e., from the adjacent regions of the advanced diffusion front; thus the "lagging" wedges of the front become closed. But when copper contains antimony, the diffusion in a lateral direction causes a widening of the "projecting wedges" of the diffusion front and this only accentuates them further in the microstructural picture.)

As has been shown by Nemnonov's study,[3] confirmed by another method in our laboratory, antimony and beryllium in copper have a similar effect on the diffusion of zinc into copper. In this instance also, the horophilic [ὅρος, boundary; φίλος, loving] nature of each of these two admixtures relative to copper (i. e., their tendency to positive intercrystalline internal adsorption) became apparent.

The aim of the present study, undertaken as the continuation and development of [previous] work,[1] was to determine the effect of small amounts of iron in copper on the diffusion of silver into copper and also the effect of the simultaneous presence of two or three admixtures (Sb + Be, Sb + Fe, Be + Fe, Sb + Be + Fe). The same metallographic method was used as in reference 1.

In the first part of the work, copper-iron alloys containing 0.001 to 0.04 percent of Fe were studied. It was found that the diffusion of silver into

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such copper is accompanied by the formation of projections of the diffusion front along the intercrystalline boundaries of the solvent metal. Here, however, the picture is different from that of the diffusion of silver into antimonial copper. When silver diffuses into copper containing iron, the projections of the diffusion front are very narrow and penetrate deeply into the copper along the grain boundaries, forming a branched lacelike network (Fig. 1), while the projections of the diffusion front of silver into antimonial copper are relatively short and wide wedges (Fig. 2).

Fig. 1. Diffusion zone in the case of diffusion of silver into copper containing 0.04 percent Fe.

Moreover, there is an important difference in the etchability and in the coloring of the projections of the diffusion front in the two cases when the etching is done by the same etchant (composition of the etchant: 10 percent ammonium persulfate and 20 percent ammonia in water). When there is antimony in the copper, the edges of the wedgelike projections become black with a tinge of brown, while the middle part of the wedges and the main part of the continuous diffusion zone take on a lighter color with a greenish tinge (the latter is usually connected with the decomposition of the solid solution of silver in copper during cooling of the sample). But when there is an iron admixture in copper, the conditions of etching being the same, the projections of the diffusion front take on a much weaker color, which is the same in the center and on the periphery (on the forward edge of the front), and in this case longer etching is required.

When silver diffuses into copper containing an admixture of iron, the projections of the diffusion front can be accounted for, as also in the case of antimonial copper, by the horophilia [surface activity] of the admixture (iron) with respect to copper, the solvent, and by the accelerating effect of iron in copper on the diffusion of silver.

Fig. 2. Diffusion zone in the case of diffusion of silver into copper containing 0.2 percent Sb.

The differences in the shape and etchability of the projections of the diffusion front in these two cases can be explained by assuming that the speed of diffusion of silver into copper depends more strongly on the concentration of iron than on that of antimony. Moreover, the silver, when diffusing into copper containing iron, advances at an accelerated rate along the intercrystalline zones which are highly enriched with respect to the horophilic iron; however, the possibilities of diffusion of silver from these zones in lateral (perpendicular) directions into the grain are limited, since the concentration of iron falls off rapidly in these directions, and its accelerating effect on the diffusion of silver is correspondingly diminished. Under these conditions, a long and narrow projection of the diffusion front is formed along a grain boundary. The concentration of silver is high only in the very narrow axial portion of the projection and drops sharply toward the edges; therefore the projection becomes etched only weakly.

The result of our attempt to find a difference in the diffusion rates of silver in copper-iron solid solutions with varying concentrations of iron was negative: there proved to be no substantial differences. This fits in with the conjecture just expressed: iron has a noticeable accelerating effect on the diffusion of silver into copper only when it is present in high concentrations. Generally speaking, the concentration of a horophilic element in the intercrystalline transition zone can exceed its solubility within the crystallite (at a given temperature). Therefore, even though the average concentration of iron in a solid solution of iron in copper is close to the solubility of iron (generally speaking, quite low), there still will be no noticeable acceleration in the advance of the continuous diffusion zone during the frontal diffusion of silver.

Table I. Type of diffusion front in the case of diffusion of silver into an alloy of a given composition at 500 degrees for 80 to 120 hours.

Admixture content in alloys under study (base, copper), percent			Equivalent to the case of diffusion of silver into copper containing:
Sb	Be	Fe	
0,2	—	0,004	Fe
0,2	—	0,001	Sb
—	0,02	0,008	Fe
—	0,2	0,040	Fe
0,2	0,2	0,001	Sb
0,1	0,2	0,001	Be
0,2	0,2	0,004	Fe
0,2	0,2	0,040	Fe
0,5	—	0,004	Sb
—	0,5	0,004	Intermediate between Fe and Be, similar to Sb

Control experiments showed that even when silver diffuses into copper which is saturated with iron, the projections of the diffusion front continue to form. This shows that the concentration of iron in the intercrystalline zone, produced by internal adsorption, exceeds the solubility in the crystal lattice. On the other hand, if the concentration of the admixture in the boundary zone (produced by internal adsorption) is close to the solubility within the crystal, then, when the alloy as a whole is saturated, the concentration becomes uniform throughout the crystals and in the boundary zones, and the diffusion front becomes completely smooth, as in the case of the diffusion of silver into a copper-antimony alloy.[1]

Thus, from the standpoint of metallography, the effect of each of the three horophilic admixtures studied (Sb, Be, and Fe) on the frontal diffusion of silver into copper manifests itself very differently. In the case of beryllium, the silver diffusion front is even, without projections, and the average width of the diffusion zone is considerably smaller than in pure copper without admixtures (the more so, the finer are the grains of copper). In the case of antimony, the diffusion front has short, wedge-shaped projections, strongly colored by a persulfate etchant. Finally, in the case of iron, the silver diffusion front has long, less strongly etching projections.

In view of the distinctly different characteristics in the microstructural picture of the diffusion of silver in the presence of one or another of these three horophilic admixtures, it seems possible that, by inspecting this picture, one might study the behavior of two or three of these admixtures when they are present in copper simultaneously. It may be assumed that different horophilic elements have different "degrees of horophilia" with respect to the same solvent; i. e., that, by enriching the intercrystalline transition zones, they lower to different degrees the surface energy of the solution, or, to be more accurate, the excess energy of these zones. Thus, a sort of "competition" is possible among the different horophilic admixtures simultaneously present in the same solid solution. This competition may result either, at a certain ratio of the average concentrations of the admixtures, in the complete displacement of one admixture by another from the zones of adsorptional enrichment, or, at other ratios of the concentrations, in the joint enrichment of the zones by the admixtures. Since the internal adsorption of various admixtures affects the properties of an alloy differently, a general formulation of this problem acquires theoretical and practical importance. We have attempted to approach the solution of this problem in the particular case of the above-mentioned horophilic admixtures (Sb, Be, and Fe) in copper.

We experimented with the diffusion of silver into copper samples containing various combinations of admixtures with different concentration ratios. Table I gives the composition of the alloys studied and the nature of the metallographic picture of the diffusion front corresponding to the three above-mentioned types. The experiments show, that, for every given concentration ratio of the horophilic admixtures, the nature of the silver diffusion is mainly affected by one of the admixtures. Consequently, for every qualitatively and quantitatively different combination of admixtures studied, one of the admixtures predominates in the internal intercrystalline adsorption. However, instances of the joint adsorption of different admixtures are possible when their effects (in the present case, on the diffusion of silver) are added, as was particularly apparent in copper with 0.5 percent of Be and 0.004 percent of Fe; the beryllium only partially eliminated the accelerating effect of iron on the diffusion of silver along the grain boundaries, but nevertheless lowered it considerably.

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[1] V. I. Arkharov and T. Yu. Goldshtein, Doklady Akad. Nauk SSSR, 66, 1113 (1949); Trudy Inst. Fiz. Metal. Ural. Filial, Akad. Nauk SSSR, issue 11, 81 (1950).

[2] V. I. Arkharov, Trudy Inst. Fiz. Metal. Ural. Filial, Akad. Nauk SSSR, issue 8, 54 (1946); issue 12, 94 (1951).

[3] S. A. Nemnonov, Trudy Inst. Fiz. Metal. Ural. Filial, Akad. Nauk SSSR, issue 11, 90 (1950).

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Received January 12, 1953; presented by Academician I. P. Bardin January 12, 1953