NATURE OF THE STRENGTH AND CERTAIN GROWTH CHARACTERISTICS OF MIXED METAL WHISKERS

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ABSTRACT: A growth mechanism is proposed and an explanation is offered of the nature of the high strength of mixed metal whiskers obtained by reduction of a mixture of the salts CuCl and $FeCl_2$. It is shown that in the process of growth of such crystals nonequilibrium capture of iron takes place, together with formation of a layer of supersaturated solid solution of iron in copper, upon the degree of decomposition of which, under certain conditions, the strength of the crystals depends. The high strength and rate of hardening are explained by the conversion of γ-Fe to α-Fe in plastic deformation. The proposed growth mechanism is in good agreement with experiment.

A number of studies has been devoted to mixed metal whiskers [1-6]. Great interest attaches to the results of investigations of the mechanical properties. Thus, in certain cases, the ultimate tensile strength of Cu-Fe crystals exceeds 200 kg/mm^2. We have attempted to explain the high strength and certain features of the growth of these crystals.

The proposed growth mechanism is based on the following assumptions.

1. At any moment, the reaction zone consists of three regions (Fig. 1): region 1, where reduction of $FeCl_2$ takes place; region 2, where both salts are reduced; and region 3, where only Cu_3Cl_3 is reduced (the main component of the vapor phase above molten CuCl at the temperatures used for obtaining mixed metal whiskers). It is assumed that there are two reasons for this. First, the significant difference in the reduction reaction equilibrium constants:

$$K_1 = \frac{[pHCl]^3}{[pCu_3Cl_3][pH_2]^{3/2}} = 8 \cdot 10^2$$

for

$$Cu_3Cl_3(g) + {}^3/_2\, H_2(g) = 3HCl(g) + 3Cu(s),$$

$$K_2 = \frac{[pHCl]^2}{[pFeCl_2][pH_2]} = 3.3$$

for

$$FeCl_2(g) + H_2(g) = 2HCl(g) + Fe(s).$$

Second, the fact that the stream of gas is impoverished in H_2 and enriched in HCl as it penetrates further into the reaction zone.

In the above formulas (g) denotes the gaseous, (s) the solid state, and p the partial pressure. The gases are assumed to be perfect. The data required for the calculation of the constants were taken from [7-9]. The constants were computed for a temperature of 1000° K. In converting these data to a temperature 1000° K the heat of the reaction $3Cu(s) + {}^3/_2Cl_2(g) = Cu_3Cl_3(g)$ in the temperature interval 1000-1300° K was assumed to be independant of temperature.

2. With time the liquid phase in the boat is impoverished in CuCl and enriched in $FeCl_2$. The vapor pressures of $FeCl_2$ and Cu_3Cl_3 are approximately the same at 1000° K ($2.4 \cdot 10^{-2}$ and $1.8 \cdot 10^{-2}$ m, respectively [7]). If it is assumed that the salts are infinitely soluble in each other in the liquid state, that the partial pressures of the vapor components above the salt mixture obey Raoult's law, and that the diffusion and condensation coefficients are roughly the same for $FeCl_2$ and $CuCl_3$, then the increase in the rate of evaporation of CuCl from the mixture may also be due to the fact that the surface on which $pFeCl_2 = 0$ is further from the surface of the fused salts than the surface at which $pCu_3Cl_3 = 0$ (see [10]).

3. A decrease in the CuCl content of the salt mixture leads to a displacement of the boundaries between regions, so that they approach the surface of the fused salts.

From assumptions 1-3 it follows that if the conditions for obtaining whiskers are such that at the initial moment the boat is in region 3 of the reaction zone, copper whiskers will grow at the walls, as when pure copper whiskers are obtained by reduction of the halide [11]. When, as a result of the displacement of the boundaries between regions, the growing crystal falls in region 2, condensation of iron as well as copper atoms takes place. There is formed a layer of solid solution of iron in copper with a concentration that varies along the radius, since, pFe(g)/pCu(g) at a given point, increases with the displacement of the boundaries. A further increase in pFe(g)/pCu(g) may lead to the formation of a mixture of small iron crystals in a single crystal of copper. When the crystal moves into region 1, the outer layer consisting of iron begins to grow. A reduction in the initial ratio $(FeCl_2)$: (CuCl) should lead to a decrease in the number of outer layers. Inner layers may also be absent, if the growth of the crystal began in region 2 or 1.

The difference in the lattice parameters for Cu and γ-Fe is such that the alloy Cu-Fe is probably one of the type that gives satellites on the roentgenograms upon aging (see, for example, the review [12]). From the data of [13], it follows that during aging the maximum hardness of the alloy Cu-2.5% by wt. Fe is reached in the initial stage of decomposition of the solid solution, long before the appearance on the roentgenograms of γ-Fe lines, i.e., apparently in the stage of formation of either a modulated structure or zones of almost spherical shape. When γ-Fe lines appear on the roentgenograms, the hardness falls to the level of the annealed alloy. Thus, the presence of a mechanical mixture of iron in copper, even if finely dispersed, does not explain the high strength of mixed whisker observed in a number of cases.

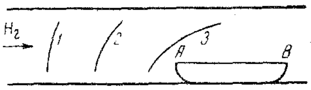

Fig. 1

The observed values of the strength may be explained by assuming that in the process of crystal growth in region 2 nonequilibrium capture of iron by copper occurs together with the formation of a supersaturated solid solution.

In a number of studies (in particular, in [13]) it has been shown that the conversion of γ-Fe to α-Fe in Cu-Fe alloys rich in Cu takes place rather easily during plastic deformation. Probably, this conversion and the associated appearance of internal stresses due to volume changes also explains the high rate of hardening during deformation of Cu-Fe mixed whiskers and their strength (naturally, at the optimal size of the precipitates formed upon decomposition of the supersaturated solid solution).

Nonequilibrium capture is possible [14], given a sufficient vapor pressure of the iron in the gas phase surrounding the growing crystal, if its its radial rate of growth v is not less than D/h (where D is the coefficient of diffusion of iron in copper, and h is the thickness of the deposited layer in laminar-spiral crystal growth). According to the data of [15]

$$D = 1.4 \exp(-51800/RT)\ \mathrm{cm^2/sec}$$

(R is the universal gas constant in cal/mole · degree). For $h = 10^{-7}-10^{-6}$ cm and T = 1100° K we found $v = D/h = 10^{-3} - 10^{-4}$ cm/sec.

The experimentally determined value of the rate* of radial growth

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*I. M. Kop'ev, Study of the Preparation, Growth Kinetics, and Strength Properties of Whiskers, Author's abstract of candidate's dissertation, Baikov Institute of Metallury, Moscow, 1963.

of copper whiskers was (1–5) · 10^{-4} cm/sec at 650° C; however, the ratio of partial pressure of the copper and iron vapor in the gas phase surrounding the growing crystal varies within wide limits with displacement of the boundaries between regions. Thus, the assumption of the possibility of nonequilibrium capture of iron by copper is perfectly justified.

Accordingly, the strength of mixed whiskers must depend on the relative thickness of the layer of supersaturated solid solution, the concentration of iron in it, and the time spent at the reduction temperature. The greatest strength will be possessed by whiskers whose growth began and continued under conditions favorable for the nonequilibrium capture of iron by copper. The maximum diameter of crystals with the greatest strength is limited by the fact that their time must be no greater than the time required to obtain a favorable structure during aging. This, evidently, is one of the most important obstacles to the use of the method of reduction of mixtures of halide salts to obtain massive specimens with strength close to the maximum values obtained for mixed whiskers.

The observed dependence of whisker strength on diameter [5, 6] must become weaker with increase in the time spent at the preparation temperature. When this time is very great (compared with the time required to obtain maximum hardness of the supersaturated solid solution), the strength will be determined by the preparation temperature, composition, and cooling conditions. On the latter depends the degree of aging of the solid solution saturated at the preparation temperature.

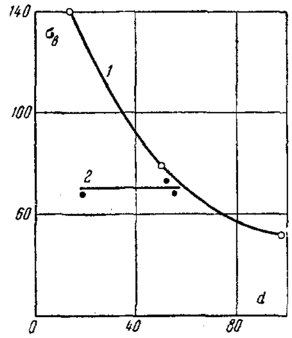

Fig. 2

In order to test the proposed explanation and obtain new data we carried out a series of experiments.

The whiskers investigated were obtained under the following conditions: reduction temperature 800°C, ratio by weight (CuCl) : ($FeCl_2$) = 1 : 0.8 (4 and 3.2 g), rate of flow of hydrogen 10 l/hr. For cooling, the boat was moved from the hot zone of the quartz tube (diam. 45 mm, length 1000 mm) to the cold zone. The cooling conditions were the same for all the specimens investigated. Otherwise the method was the same as that described in [6].

The crystals were subjected to X-ray analysis at different stages of their growth, 5, 10, 13, 16 min after the beginning of the reduction process; the total reduction time for the weights of salts employed was 15–16 min; rotation roentgenograms were obtained in chambers 57.3 mm in diameter. The emission of a Co-anode was used; this ensured good enough accuracy of determination of the lattice parameter (doublet (400) of copper in this radiation is obtained at angles greater than 80°).

Roentgenograms of crystals taken from boats held in the reaction zone for 5 min show only distinct spots of copper, whose lattice parameter is equal to 3.6090 ± 0.0005 kX.

Some of the crystals from boats held in the reaction zone for 10–16 min also give only copper spots on the roentgenograms, but those at larger angles are blurred and displaced in the direction of smaller angles. The maximum value of the lattice parameter determined from the position of the center of gravity of the photometric curve of the spot (400) $K_{\alpha 1}$ on these roentgenograms is 3.614 ± 0.001kX. The blurring of the spots is probably connected with inhomogeneity of the solid solution along the crystal radius. If this is so, then the greatest concentration of the solid solution obtained under these conditions corresponds to a value of the lattice parameter greater than 3.614 kX. After such crystals have been held at 800° C for 10 hr, the spots become distinct; in this case the lattice parameter of copper does not exceed 3.6098 ± 0.005 kX.

In the roentgenograms of crystals taken at the edge A of boats held for 16 min in the reaction zone there are, apart from copper spots, spots of α-Fe. Some of these crystals are covered with a layer of iron. The lattice parameter of copper after annealing of these specimens for 10 hr is 3.6098 ± 0.0005 kX. This value probably corresponds to a saturated solution of iron in copper at the preparation temperature (about 1 at.-% [16]).

Comparison of the data obtained and the results of a determination of the dependence of the lattice parameter on the concentration of the solid solution of iron in copper [16] shows that the value 3.614 kX corresponds to an iron content in the solid solution appreciably exceeding the equilibrium value at the preparation temperature.

We also investigated crystals grown on a copper plate placed outside the boat. When the boat was held in the reaction zone for 16 min the crystals on these plates furthest from the edge A in a direction opposite to the direction of flow of the gas show only α-Fe spots on the roentgenograms.

The results of the X-ray analysis therefore confirm the correctness of our assumptions concerning the growth mechanism of mixed whiskers and the possibility of formation of a layer of supersaturated solid solution as a result of the nonequilibrium capture of iron by the growing crystal. These results also show that under the conditions employed the boat initially lies completely in region 3 of the reaction zone. On completion of the reaction zone. On completion of the reduction process, edge A of the boat is in region 1.

The results of mechanical tests shown in Fig. 2 are in good agreement with the proposed explanation of the strength of mixed whiskers. Here σ_b is the ultimate tensile strength in kg/mm^2, d is the diameter of the crystals in microns. Curve 1 was obtained for crystals taken from boats that had spend 16–18 min in the reaction zone; curve 2 for crystals from boats kept for 10 hr at the preparation temperature. Both curves were drawn through the three points representing the highest results of those obtained in testing 40 specimens in each batch.

The use of the results presented in [1–5] for verifying the above assumptions is seriously complicated by the fact that none of these papers gives the time spent by the crystals at the reduction temperature, while the range of temperatures employed is quite wide. In [6] a considerable part of the result was obtained on crystals held at the preparation temperature for 2 hr; however, certain results (in particular, the results of mechanical tests) were obtained for much shorter periods, though this was not taken into account in assessing the results. The segmental crystal growth observed in [3] is evidently connected either with instability of the temperature or hydrogen flow during preparation of the crystals or, as assumed in [5], with multiple repetition of the reduction process. Accordingly, the results obtained in [1–6] do not contradict our proposed growth mechanism and explanation of the strength of mixed whiskers.

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