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INTERGRANULAR CORROSION OF HIGH-PURITY ALUMINUM IN HYDROCHLORIC ACID

II - GRAIN-BOUNDARY SEGREGATION OF IMPURITY ATOMS

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SUMMARY

The variation in the rate of intergranular corrosion of single-phase high-purity aluminum in 20 percent hydrochloric acid as a function of iron content and final-annealing temperature is attributed to the segregation to atomic sites in the grain-boundary region of iron and possibly other impurity atoms. The experimental results are analyzed by reference to a distribution function, obtained by statistical mechanical methods, which gives the equilibrium fraction of certain sites in the boundary which are occupied by solute atoms in terms of the interaction energy for the segregation of the solute atoms at these sites. Segregation of iron alone cannot account for the observed results; from consideration of the atomic sizes and the quantities of other impurities present, it is expected that copper is also involved. The observed relative corrosion rates can be represented as due principally to differences in the fraction occupied by iron and copper atoms of those boundary sites where the potential energy of interaction for the segregation of iron or copper is at least as large as -0.7 electron volt (-16,000 calories per mole) and perhaps as large as -1.0 electron volt (-23,000 calories per mole). Since energies of this magnitude cannot be accounted for by the loss in lattice distortional energy when an undersize iron or copper atom is replaced by an aluminum atom at a grain-body site, a substantial contribution to the potential energy of interaction must come from a reduction of the local energy about the site in the boundary. It is believed that metals and alloys generally contain an alloying element or impurity the atoms of which have a considerable tendency to concentrate in the boundaries but that the effect on the properties of the boundaries will be apparent only under special conditions.

INTRODUCTION

A previous report describes a study of the intergranular corrosion of high-purity aluminum in hydrochloric acid (ref. 1). Among other things, it was found that the rate of intergranular corrosion in specimens annealed at temperatures within the single-phase region and then rapidly quenched was dependent on the final annealing temperature and on the impurity content of the material. The effects of temperature and purity on the corrosion rate were attributed to the segregation of iron and possibly other impurity atoms to atomic sites in the grain boundaries of the specimen. A more detailed analysis of this segregation has been made possible by additional observations with closer control of certain factors; this work is described in the present report. Some of the conclusions were mentioned in the previous report.

Impurity or solute atoms whose effective size differs appreciably from that of the solvent atoms are expected to have a tendency to segregate in the grain boundaries because the boundary (i.e., the transition region several atomic diameters thick between adjoining grains) does not have the regular structure of the normal lattice and the volume per atomic site varies so that there will be sites at which the solute atom is accommodated better than at a normal lattice site, as first suggested by McLean (ref. 2). The substitution of an atom of different size may also operate to reduce the local energy through the removal of a solvent atom constrained to occupy an abnormal volume and the reduction of the forces acting on its neighbors in the boundary. The most direct evidence for the occurrence of this segregation has been obtained for very small amounts of polonium in lead-bismuth alloys by an autoradiographic method (ref. 3). Some of the other systems in which recent evidence of this phenomenon exists have been listed by Perryman (ref. 4) who also studied the intergranular corrosion of high-purity aluminum and concluded that there was a tendency for iron atoms to segregate at the grain boundaries.

The segregation of substitutional atoms in the boundaries is considered from the viewpoint of statistical mechanics from the model of solute atoms distributed among sites of different potential energy. The difference between the energy associated with the presence of the solute atom at a site in the boundary and at a site in the grain body is the interaction energy, which has a negative value for those sites at which segregation tends to occur. At equilibrium at any temperature, the fraction of boundary sites of a given interaction energy which are occupied by solute atoms is a certain multiple of the fraction of grain-body sites occupied by solute atoms, the latter fraction being practically equal to the over-all atomic concentration. If the interaction energy only varies slowly with temperature (as may be expected when relative atomic size is the principal factor), then the concentration of solute atoms in the grain-boundary region is higher the lower the temperature. Thus, so far as the boundaries are concerned, the effect of lowering the temperature is the same as the effect of raising the over-all solute content. If the rate of intergranular attack depends essentially on the concentration of solute atoms in the boundaries and not on the over-all solute concentration, as may be the case when the solute is present in small amounts as an impurity having a strong tendency to segregate, the interaction energy can be determined by matching the corrosion-rate data for different annealing temperatures and impurity contents.

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SYMBOLS

$A = c \exp\left(-G_i/kT\right)$

c	over-all atomic concentration of solute
E	potential energy of interaction
ΔF	molar free energy change
G_i	interaction energy
g_i	number of boundary sites at which interaction energy is G_i
K	equilibrium constant
k	Boltzmann constant
M	metal atom
N	number of atomic positions
N'	number of solute atoms
R	gas constant per mole

ΔS_v	change in vibrational entropy
T	absolute temperature
T_m	absolute melting temperature
X_1,X_2	defined by equations (3)
x_i	fraction of g_i occupied by solute atoms
β	constant determined from measured temperature dependence of one of single-crystal moduli
$\prod\limits_{i}$	iterated product

EXPERIMENTAL PROCEDURE

The experimental procedure has been described in detail in reference 1. Briefly, the rate of intergranular attack was observed in 1/4- by $1\frac{1}{2}$-inch specimens of 0.064-inch high-purity aluminum sheet etched lightly and totally immersed in 20 percent hydrochloric acid containing about 0.1 part per million of residual copper. The specimens were annealed in air at temperatures within the single-phase region and quenched in cold water to preserve the structure characteristic of equilibrium at the final annealing temperature. The material used consisted of three compositions, essentially differing only in iron content, of -H18 high-purity aluminum sheet prepared by the Aluminum Company of America. The analyses are given in table I. The temperatures of treatment ranged from near the melting point (647° C) down to minimum temperatures substantially above the iron solvus temperature for each composition. Although several types of annealing schedules used to compare the structures produced at different temperatures gave similar results in previous studies, it was considered that the most unambiguous indication of the effect of temperature would be given in specimens initially treated at 647° C and either quenched or furnace cooled to a lower temperature, held, and quenched. This minimizes differences in grain size and tendency toward preferred orientation for different final temperatures of treatment. The specimens were held for 24 hours at 647° C; at lower final annealing temperatures the holding time was increased by 24 hours for each 50° C below this temperature.

COMPARISON OF GRAIN SIZE AND ORIENTATION DISTRIBUTIONS

In order for the comparison of intergranular corrosion data for different purities and final annealing temperatures to be valid, it was necessary to make certain that all samples were similar in several characteristics. These are discussed below.

In previous work, the rate of intergranular attack had been measured by the time required for one or a few grain boundaries to be corroded through the thickness of the sheet. For the present work, a more satisfactory measure of the over-all corrosion rate was provided by following the number of individual boundaries corroded through as a function of time, as determined by momentarily removing the specimen from the test beaker and holding it up to a strong beam of light in a darkened room. Three or more specimens of each composition were prepared for each heat treatment. There were no substantial consistent grain-size variations between specimens of different purity; allowance for the variation in grain size from specimen to specimen was made by taking for comparison only those specimens having approximately a standard grain-size distribution which could be chosen to include the majority of the specimens prepared. Most grains of the standard had average diameters of 2 to 5 millimeters.

It was also necessary that the various specimens to be compared should contain about the same proportion of those boundaries which have little susceptibility to attack, such as boundaries between grains of nearly the same orientation and coherent twin boundaries. These are the boundaries of low relative interfacial energy, consistent with the view (refs. 1 and 5) that the susceptibility of this material to intergranular attack in 20 percent hydrochloric acid is related to the abnormal structure and energy of the grain-boundary region, the free energy of which is higher than that of the grain body because of the contribution of the interfacial free energy. It has been shown by Friedel, Cullity, and Crussard (ref. 6) that the relative interfacial energy of a grain boundary in high-purity aluminum does not for the most part vary greatly with orientation difference and is substantially lower than the energy of a general grain boundary only for low-angle boundaries (orientation difference of less than 7°) and for boundaries between grains where there is an approximation to a (100), (110), or (111) plane of symmetry and the boundary lies in the plane of symmetry.

Except for two doubtful cases, which were discarded, the presence of numerous clusters of grains having nearly the same orientation or of a pronounced tendency toward preferred orientation was not observed on visual examination of the reflections of a beam of light from the surfaces of the specimens as etched by the test acid. This was verified for samples of compositions I and III by determining the orientations of a group of grains from back-reflection Laue photographs. The orientations, as plotted within a single stereographic triangle, are given in figure 1. Low-angle boundaries together with those medium- and high-angle boundaries which approximately fulfilled the symmetry conditions for low interfacial energy constituted roughly one-fifth of the total number in each group and were in about the same proportions in compositions I and III. On the basis of these observations, it is presumed that the distributions of grain orientations in the three compositions studied in this work may be taken as similar so far as susceptibility to intergranular corrosion is concerned.

An additional point concerns the greater number of boundaries with noticeable curvature exhibited by specimens treated only 24 hours at 647° C as compared with specimens quenched from lower final annealing temperatures where the total annealing period was much longer. These differences in boundary curvature did not appear to have had significant effects on the over-all corrosion rates since extending the annealing period to 96 hours for samples quenched from 647° C produced boundaries comparable in straightness with those characteristics of long annealing times at lower final temperatures but did not result in corrosion rates significantly different from those of the 24-hour specimens (occasional small differences in grain size being taken into account). From the viewpoint of relative interfacial energy, the curvature would be expected to be significant only in those boundaries where there is symmetry about one of the three minimum-energy planes and the boundary lies near this plane since, under these conditions, a straight boundary could be one of low energy, but a substantial portion of a curved boundary would always have close to the full energy of a general boundary.

EXPERIMENTAL DATA

The rate of intergranular corrosion in 20 percent hydrochloric acid as a function of iron content and final annealing temperature is shown in figure 2 where the number of individual grain boundaries corroded through the thickness of the specimen with time has been averaged for the several samples of each type suitable for comparison. In composition III, the iron solvus temperature is too close to the melting point to permit variation of the final annealing temperature; the temperature dependence for composition I is described below.

The scatter of the data for the samples of each type was moderate, even including those exposed at different times, compared with the differences between the averages for the various types, as has been indicated in figure 2 by giving for composition II as quenched from

647° C the range of results from three to four samples representing tests run at three different times.

In the series of tests on composition I quenched from several final annealing temperatures, the corrosion tests were accidentally exposed to unusually low temperatures (10° to 15° C) from the first to the fourth day. At these temperatures, the evolution of hydrogen from the corroding boundaries had practically ceased and corrosion progressed very slowly. On the fourth day, the temperature was brought within the usual range of 22° to 26° C and the test allowed to continue. It was found that the effect of the cold period on the curve for the samples quenched from 647° C had been principally to shift it 2 days to the right of the curve shown in figure 2 for independent tests on similarly treated samples. The curves for the 575° and 500° C samples could be assumed to have been affected in a similar manner, the approximate correctness of this assumption being established by reference to previously obtained data on samples of composition I quenched from 500° or 600° C after an initial quench from 647° C. The corrosion rate of composition I as a function of final annealing temperature is shown in figure 3, the curves of which may be approximately compared with the curves of figure 2 by taking the zero of time in figure 3 at 2 days. The corrosion rate of composition I is seen to vary slowly with temperature as compared with composition II. The uncertainties in the data for composition I at 575° and 500° C were not sufficient to introduce uncertainties in the interpretation of the results.

Visual observation of the specimens during the corrosion tests had indicated that the differences in corrosion rate shown in figure 2 represented, at least in part, differences in the rate of progress of intergranular penetration and not merely differences in an induction period before the beginning of rapid penetration. To examine this more closely, a number of specimens of compositions I and III quenched from 647° C were exposed unetched to the test acid, and after appropriate intervals a sample was withdrawn, copper plated, embedded in a plastic mount, and sectioned. Previous work (ref. 1) had established that the rate of intergranular attack in these specimens is not substantially altered if the light preliminary etch is omitted. In both compositions, there was an initial period in which intergranular penetration was slow leading to the final period during which the rate of penetration was roughly constant. Although the polished section provided too small a sample of the total number of boundaries in the specimen to establish the duration of these periods precisely, the observations indicated that the initial period usually lasted several days and was shorter for the more active boundaries. In composition I, for example, the initial period appeared to be about 1 day for boundaries corroding through in 4 days and 2 (occasionally 3) days for boundaries corroding through in 6 or more days. In composition III, the initial period was perhaps 2 to 4 days for boundaries corroding through in 12 to 16 days. Thus, the differences in corrosion rate between these two cases are primarily differences in the rate of progress of intergranular penetration, and the same may be expected with respect to the other cases of intermediate corrosion rate.

In figure 2, the values for composition III have not been carried beyond 16 days because then the general corrosion was sometimes such that it was difficult to make a reliable estimate of the number of boundaries corroded through by intergranular attack alone without appreciable aid from general or local thinning. The greater tendency of composition III to general corrosion is believed due to residual composition gradients in the solid solution and is thought to have had no substantial influence on the rate of intergranular corrosion (ref. 1). In general, the behavior of specimens of different purity was basically similar in every respect except for the rate of corrosion.

That the over-all corrosion rates of specimens of differing purity and final annealing temperature can be matched directly or by interpolation is seen from figure 2 where the data yield a single family of curves. The validity of the projected determination of the interaction energy for the segregation of impurity atoms by the matching procedure requires that the corrosion rate be dependent only on the concentrations of impurity atoms in the boundaries and therefore independent of over-all (i.e., grain body) impurity content. That this may reasonably be presumed may be seen from the observation that the difference of solution potential in 20 percent hydrochloric acid between the grain bodies of compositions I and III is only 1 millivolt and this will be small relative to the difference of potential which must exist between the boundaries and bodies of any one specimen in order to produce the observed susceptibility to intergranular attack. Further, this presumption is not required to hold closely for composition III, the corrosion rate of which lies in a range where this rate appears to be relatively insensitive to changes in certain parameters, as indicated by the small change in the corrosion rate of composition II between 600° and 550° C and hence can be only of limited use in determining the interaction energy.

It may be noted that, provided this one condition is satisfied, the interaction energy may be determined from data obtained under any sufficiently sensitive conditions of corrosion without consideration of the behavior in other corrodents or of the mechanism of corrosion.

DISCUSSION

First, a discussion will be given of the considerations on which the analysis of the segregation of impurity atoms is based.

Grain Boundary Structure and Tendency for Segregation

The lattices of adjoining grains of different orientations cannot in general be in register at their boundary, and there will be a region where the positions of the atoms form the transition from one lattice to the other. The grain-boundary region is considered to consist of a central portion of irregular structure, perhaps three atom planes in thickness, where the atoms have definite positions even though these do not correspond to the positions of either lattice, together with narrow fringes where the remainder of the transition is accomplished by "elastic" distortion of the normal lattice. By analogy with an edge dislocation, the central portion of the boundary may be considered its "core" while the fringes correspond to the region where the stress field of the dislocation is appreciable. While in a very low angle boundary, which may be regarded as a wall of separated edge or screw dislocations, the stress field is appreciable in magnitude at small distances from its core; with larger orientation difference the stress fields of adjacent dislocations annul each other at very small distances from the center of the boundary so that the fringe of a medium- or high-angle boundary extends at most for a few atom planes and it cannot be described in terms of stress.

Several factors may contribute to the tendency to segregate in the boundary region of substitutional solute atoms whose sizes differ from those of the solvent atoms. Because of the nonregular structure of the boundary core, the volume per atom varies so that there will be sites at which the solute atoms may be placed with less misfit than at sites in the body of the grain. Also, the atoms at these sites in the boundary core have abnormal distance relations with their neighbors which lead to high local energies; the replacement of such atoms by solute atoms of appropriate size may involve a substantial reduction of the local energy. Segregation of an atom of appropriate size will lower the strain energy in a region where a stress having a hydrostatic component exists (ref. 7) and thus may be expected, for example, at a low-angle tilt boundary composed of edge dislocations.

The importance of the relative size factor is shown, for example, by Hume-Rothery's rule that elements differing by as much as 15 percent in atomic diameter generally form solid solutions only of very limited extent. If the size difference is a deterrent to solubility, then it may be anticipated that the solubility will be greater at atomic sites of more favorable size, and these sites then tend to be occupied preferentially. However, other factors besides relative size may have important influences on the tendency for segregation. For one thing, the Brillouin zone structure of the normal lattice does not hold for the boundaries. If free-electron theory is used to approximate the valence electron energies in the boundaries, the densities of electronic states are lower in the boundaries, as shown by the calculations of Matyáš for the aluminum face-centered cubic lattice plotted in reference 8; thus, the presence of a solute of valence different from that of aluminum produces a larger change in the Fermi energy of the boundary than of the grain body. In addition to the electronic relations, the electrochemical relations between the solute and solvent may be different in the boundary where the number and distance of nearest neighbors differ from those of the normal lattice. For these reasons, the evaluation of the tendency for segregation in terms of size difference alone must be considered incomplete although it is perhaps justifiable as an approximation when the size difference is substantial.

The best measure of the effective size of a solute atom is the "apparent atomic diameter" which has been obtained for several solutes in aluminum by Axon and Hume-Rothery (ref. 8) by extrapolating to 100 percent solute the initial portion of the plot of lattice parameter versus atomic concentration of solute. The apparent atomic diameter is a measure of the average distortion produced in the solvent lattice; the local distortion in the immediate vicinity of each solute atom will be greater. Solutes of valence different from aluminum tend to alter the aluminum lattice parameter because of the change in the extent of the Brillouin zone overlap, and where the volume per valence electron differs sufficiently from that of aluminum the apparent atomic diameter of the solute may differ appreciably from its elemental atomic diameter (ref. 8). The effect on the aluminum lattice produced by alteration of the electron-atom ratio may be expected to be more uniformly distributed over the lattice than the distortion produced by differences of inherent (i.e., ionic) size and thus would be less effectively relieved by segregation of the solute atom to the boundaries where, although the volume per atom varies, the volume averaged over several atoms is probably close to the normal atomic volume of aluminum. It may be anticipated that the relative size factor as related to the tendency for segregation cannot always be judged merely by comparison of the apparent atomic diameter of the solute and the elemental atomic diameter of aluminum.

Distribution of Solute Atoms

The solute atoms under consideration tend to migrate to positions in the grain boundary, thereby lowering the potential energy of the system, and at the same time thermal agitation tends to scatter them throughout the metal. To obtain the equilibrium distribution, a total of N' solute atoms and a fixed number N of atomic positions is considered, each position occupied either by a solvent or a substitutional solute atom. In the volume of polycrystalline metal under consideration, there will be a certain number g_i of boundary sites at which the energy of interaction is G_i, a fraction x_i of these sites being occupied by solute atoms. The quantity G_i is the increase in energy when a solute atom in the grain body changes places with a solvent atom at one of the g_i sites and includes a term due to the change in vibrational entropy. Each g_i is an unknown but fixed number which is determined by the structure of the specimen. It is assumed that the solute atoms in any cell (i.e., in the boundary) do not interact strongly with each other. Then there are $\prod_i N'!/(g_i x_i)!$ combinations by which the N' solute atoms can be taken $g_i x_i$ to the ith cell and $\prod_i (N - N')!/(g_i - g_i x_i)!$ combinations by which the N - N' solvent atoms can be placed in the remaining sites. This leads to a distribution function in which g_i does not appear,

$$x_i/1 - x_i = \left[c/(1 - c)\right] \exp\left(-G_i/kT\right) \tag{1}$$

where c is the over-all atomic concentration of the solute, k is the Boltzmann constant, and T is the absolute temperature. In the present experiments, c is small and equation (1) reduces to

$$x_i/(1 - x_i) = c \exp\left(-G_i/kT\right) \tag{2}$$

The equivalent thermodynamic derivation is given in the appendix.

The various atomic sites in the grain boundary region correspond to various values of G_i. For sites of unfavorable volume, G_i is positive. At favorable sites, G_i is negative and $x_i > c$. The influence of the exponential is strong so that, if G_i has a sufficiently large negative value, these highly favorable sites may be almost completely occupied by solute atoms even when the over-all concentration of solute is small. However, it is not likely that a large fraction of the total number of boundary sites would be occupied. For one thing, only about half the grain boundary sites will be of appropriate relative size for a given solute. Further, only a portion of these sites will yield interaction energies sufficient to produce strong segregation tendencies. Although all of the most favorable sites may be able to accept solute atoms, it is anticipated that, under conditions where even the less favorable sites tend to be occupied by solute atoms, the segregated atoms will interact strongly with each other and saturation of the boundaries will occur much before all the sites of favorable size have become occupied. Both the strength of these interactions and the limiting concentration are expected to vary from one solute to another.

The energy G will contain a temperature-dependent term $-T\,\Delta S_v$ due to the change in vibrational entropy as well as the term E representing the change in potential energy when the solute atom in the grain body changes places with a solvent atom in the boundary. As shown by Zener (ref. 9), a vibrational entropy increase is associated with the presence of elastic strain because there is then a lowering of the elastic modulus and an increase in the amplitude of atomic vibration. Since the segregation of a solute atom results in a reduction of the "strain" energy both about the lattice site it formerly occupied and about the boundary site it takes, the vibrational entropy change is negative. The relation between ΔS_v and E can be roughly estimated by the method of Zener (ref. 10). On the assumption that the major part of G is strain energy and that the fractional temperature variation of G does not differ greatly from the temperature variation of the elastic moduli, the following expression is obtained for the upper limit of the vibrational entropy change:

$$\Delta S_v = \beta E/T_m$$

where T_m is the absolute melting temperature and β is a constant obtained from the measured temperature dependence of one of the single crystal moduli and has the value 0.35 for aluminum. In the 500° to 647° C range of the present experiments, the magnitude of $T\,\Delta S_v$ is, according to this estimate, three-tenths or less of the magnitude of E. It may be noted that only a small change in G is produced by the temperature variation of the vibrational entropy term over this relatively narrow temperature range.

The application of this distribution function to experimental observations of the properties of the boundaries as functions of c and T can lead to information about the energy and entropy changes accompanying the segregation of solute atoms. Information cannot be gained about the distribution of interaction energies at various sites in the boundaries, or the fraction of the total number of boundary sites which is occupied by solute atoms under given conditions, without reference to independent evidence which is not now available.

One feature of equation (2) worthy of note is the slow approach to saturation. If the right-hand member of equation (2) is represented by A, $x = A/(1 + A)$. Thus, when A is sufficiently large and x is a sufficiently large fraction, changes in the experimental conditions which increase A (i.e., favor increased segregation), for example, a decrease in the temperature, produce small changes in x even for substantial changes in A.

Preliminary Analysis of Experimental Data

The important features of the experimental data presented in figures 2 and 3 may be summarized as follows:

(1) The various cases can be listed in order of decreasing rate of intergranular attack as follows: (I-647), (II-647), (I-575), (I-500), (II-600), and (II-550 and III-647).

(2) The dependence on final annealing temperature of the corrosion rate of composition I is much less than that of composition II. There is a considerable decrease in the corrosion rate of composition II in going from 647° to 600° C but only a small decrease from 600° to 550° C. This indicates either that the grain-boundary sites in composition II to the occupant of which the corrosion rate is sensitive are approaching saturation by solute atoms in the 600° to 550° C range, that the rate of intergranular attack is becoming less sensitive to further increases in the concentration of solute atoms in the boundaries, or that there is a small decrease in the interaction energy for the segregation of iron atoms in this range.

(3) The corrosion rate of composition III at 647° C matches that of composition II at 550° C. If there is either saturation or insensitivity in this range of corrosion rates, these two specimens may not reliably be considered equivalent for the estimation of the interaction energy.

The differences in corrosion rate of specimens quenched from 647° C and differing only in iron content indicate that segregation of iron atoms occurs. If only iron need be considered, expression (2) should permit the evaluation of the energy G for the grain-boundary segregation of iron atoms (at those sites to the occupant of which the corrosion rate is sensitive) under the assumption that the corrosion rate is dependent only on the concentrations of iron atoms in the boundaries, that is, on the value of x. Although the boundaries contain sites for which G varies over a wide range, it is only within a limited range of G that the observed temperature dependence of the corrosion rate can be produced since sites of too large (too negative) G are substantially saturated and of too small G substantially empty over the whole temperature range. If the data can be described in terms of a single effective G, this can be calculated from any two combinations of c and T producing the same corrosion rate. The values of x corresponding to various experimental conditions, as calculated from this G, must have reasonable magnitudes.

With this procedure, the estimation of G for the segregation of iron by matching, for example, composition I at about 500° C with composition II at 600° C yields a value of magnitude substantially above 1 electron volt. This cannot be correct since it would require the sites having this interaction energy to be practically saturated $(x > 0.99)$ in composition II even at 647° C. It is thus necessary to consider the other impurity elements which may be involved.

Of the other impurities in compositions I, II, and III, copper (0.00093 atomic percent), silicon (0.0006 atomic percent), and magnesium (0.0004 atomic percent in composition I) are the ones present in the greatest quantities. The atomic sizes of these elements are listed in table II; the only presently available information from which their relative tendencies toward segregation can be estimated is their size difference as compared with that for iron. On this basis, copper is expected to segregate about as strongly as iron, magnesium somewhat less strongly, and silicon still less. Because of the sensitivity of the extent of segregation to the value of the interaction energy, the assumption even of moderate differences of interaction energy corresponding to these differences in size leads to the conclusion that the contribution of silicon will be negligible at temperatures where substantial segregation of copper will occur. Magnesium may have a small influence in composition I. The segregation of magnesium is to sites of larger than normal atomic volume and hence it is not in competition with iron and copper for the smaller boundary sites.

The impurity elements which are present in still smaller quantities cannot produce substantial grain-boundary concentrations unless their interaction energies are very high. This is not anticipated for sodium or calcium, despite their large atomic diameters, because their ionic diameters are not large and their volumes per valence electron are much larger than that of aluminum; thus, their effective diameters as dissolved in aluminum are expected to be much closer than their atomic diameters to the size of the aluminum atom, as is the case for lithium (table II).

The experimental data will thus be considered on the basis of the simultaneous segregation of iron and copper. It can be seen that, in view of the small iron and copper contents of the material studied, the interaction energies involved must be large in order that the grain-boundary concentrations of these elements will be sufficient to produce the observed effect on the intergranular corrosion rate.

Further Treatment of Experimental Data

For simultaneous segregation of two solutes, the fractions X_1 and X_2 of grain-boundary sites actually occupied by the solute atoms can be obtained from the values of x_1 and x_2 calculated from equation (2) by solving the expressions:

$$X_1 = x_1(1 - X_2)$$
$$X_2 = x_2(1 - X_1)$$

leading to the relations:

$$\left.\begin{aligned} X_1 &= x_1(1 - x_2)/(1 - x_1x_2) \\ X_2 &= x_2(1 - x_1)/(1 - x_1x_2) \end{aligned}\right\} \tag{3}$$

Now the atomic concentrations of iron are 0.0002 percent in composition I, 0.0019 percent in composition II, and 0.011 percent in composition III. Thus, the copper content of composition I is five times and that of composition II is half the iron content. Copper cannot have considerably more influence on the corrosion rate than an equal iron content, since this would require that compositions I and II behave similarly at all temperatures which is not observed, nor considerably less influence, since a reasonable interpretation of the data cannot be given for iron alone. Iron and copper are thus taken to be inherently of approximately equal importance.

To estimate the interaction energy G for iron and copper, it is now necessary to determine what values of G are required to account for the relative corrosion rates in terms of the relative fractions of sites occupied by iron and copper atoms as calculated from equations (2) and (3) for the various specimen compositions and temperatures. It is found that, in order to represent the corrosion rates of the several specimens of composition I (where copper is the dominant solute element) in the proper relation to the corrosion rates of composition II (where iron has the greater influence), the values of G for iron and copper must be about the same; if equal concentrations of iron or copper atoms in the boundaries are not equally effective in reducing the intergranular corrosion rate, it is necessary to take the effective G slightly lower or higher for copper than for iron.

Further, the observed dependence of the intergranular corrosion rate on final annealing temperature in compositions I and II cannot be due to a considerable extent to segregation at sites where G is less negative than about -0.6 electron volt since this would require the unreasonable conclusion that the corrosion rate could be altered by a very small change (less than 1 percent) in the fraction of these sites occupied by iron and copper atoms and thus by a much smaller change in the fraction of the total number of boundary sites occupied by these atoms. For similar reasons, the principal contributions to the changes in corrosion rate with final annealing temperature cannot come from segregation at sites where G is more negative than about -0.9 electron volt since most of these are occupied by iron and copper atoms over the whole temperature range and, as previously noted, there are only small changes in x even for substantial changes in $c \exp(-G/kT)$ when x is a large fraction. The change in the fraction of occupied sites with temperature for various values of G is illustrated in table III where a comparison is made for specimens of composition II quenched from two temperatures between which there is a considerable difference in the rate of corrosion.

Consideration can now be given to the vibrational entropy and potential energy components of G:

$$\exp(-G/kT) = \exp\left(\Delta S_V/k\right) \exp(-E/kT)$$

Here $\exp\left(\Delta S_V/k\right)$ is a fraction and $\exp(-E/kT)$ a large number since both ΔS_V and E are negative. These factors have opposite effects on the extent of segregation, and the larger the assumed entropy change, the larger is the magnitude of E required to yield values of G between -0.6 and -0.9 electron volt. Since at least a small vibrational entropy change is expected, E will be at least as negative as -0.7 electron volt, corresponding to the -0.6-electron-volt limit of G. The estimate by Zener's method of the largest vibrational entropy change which may be expected is about $0.3E$ at the annealing temperatures of these experiments; this would require values of E in the range -0.9 electron volt to -1.3 electron volts. However, if the values of X corresponding to various values of E are calculated for the compositions and temperatures for which corrosion data were obtained, it is found that magnitudes of E above 1.0 electron volt do not permit a satisfactory description of the relative corrosion rates. The differences in rate of intergranular attack observed in the present study can be described as due principally to the differences in the fractions of iron and copper atoms occupying those grain-boundary sites where their potential energies of interaction are within the range -0.7 to -1.0 electron volt.

The comparison of the calculated fractions of occupied sites with the observed relative intergranular corrosion rates is illustrated in table IV for several combinations of the vibrational entropy factor $\exp\left(\Delta S_V/k\right)$ and potential energy of interaction E which yield about -0.7 electron volt for G in the temperature range studied. The entropy factors 0.25 and 0.065 were chosen because they are equivalent here to differences of about 0.1 and 0.2 electron volt in E. In view of the uncertain factors in this discussion, any one of these sets of figures is considered to provide a reasonably satisfactory representation of the relative corrosion rates. It is not possible to draw further conclusions concerning the entropy factor nor concerning G or E since other values of G in the -0.6- to -0.9-electron-volt range and of E in the -0.7- to -1.0-electron-volt range represent the relative corrosion rates about as well as the values given in table IV. That the calculated values for composition I are relatively too small at 575° C and too large at 500° C cannot be accounted for by an additional effect due to the magnesium in composition I; however, small changes with temperature in E for copper or iron could be sufficient to bring the calculated values into the correct order.

The foregoing argument has thus furnished information on one physically important quantity, the potential energy of interaction E, which has been estimated despite exact knowledge of the limitations of equation (2), of the change in vibrational entropy accompanying segregation, of the relative effects on the corrosion rate of equal grain-boundary concentrations of iron or copper, and of a possible small contribution of magnesium in composition I. Certain additional considerations are discussed in the following paragraphs. It may be stated again that the conclusions of this work apply to the general medium- and high-angle grain boundaries since it is the corrosion rates of these boundaries which were measured.

Within the range of annealing temperatures used in these experiments, the effective value of E cannot vary to a large extent. If the effective E became 0.1 electron volt less negative for each 100° C decrease in temperature, specimens of composition II would have had the same grain-boundary concentration and the same corrosion rate when quenched from either 647° or 600° C; if E became 0.1 electron volt more negative for a 100° C temperature decrease, then the temperature dependence of the corrosion rate in composition I would have been relatively much more pronounced than was observed. In this connection it is of interest to note that the atomic size difference for copper (a change of which with temperature would contribute to a change in E) is shown by the X-ray data of Ellwood and Silcock (ref. 11) for 1 atomic percent copper in aluminum to change only from 11.6 percent at 18° C to 12.4 percent at 548° C. The decrease of the elastic moduli with increasing temperature would be a more likely source of a variation of E with temperature.

The question is considered whether discrepancies in the analysis of the experimental results arise from the simplification made in deriving equation (2), that segregation has not significantly altered the grain-body solute concentration. With a specimen of 3-millimeter average grain diameter, and taking the boundary as 10 A thick and the limiting fraction of the sites of high interaction energy as 10 percent of the total, it is found that occupation of all of the high-energy sites will change the grain-body concentration of solute by more than a few percent only for solute contents less than 10^{-6}. The uncertainties due to this simplification are therefore negligible for the iron and copper contents involved in this work.

It may be noted that knowledge of the relative effectiveness of equal boundary concentrations of different segregated solute atoms, not provided by the present study, would indicate the reason for their effect on the intergranular corrosion rate in hydrochloric acid of this concentration. If they are effective because they reduce the local energy in the boundary, the effect should depend on relative size and all segregated solutes should decrease the rate of attack. If, however, the segregated atoms produce their effect by increasing the alloy content of the grain-boundary material and thus by shifting its solution potential relative to that of the grain body, then the specific properties of the solute atom are involved and solutes of the same size may have widely different effects and may increase as well as decrease the corrosion rate.

Significance of Potential Energy of Interaction

The interaction energy for the segregation of a solute atom can be estimated from the formula of Cottrell (ref. 7) for the interaction with the stress field of an edge dislocation. Since the combination of dislocations into boundaries results in a certain cancellation of the opposing stress fields of adjacent dislocations, this energy will give an upper limit to the potential energy of interaction of the solute atom at sites in the fringes of the boundary. The estimate for iron or copper atoms in aluminum shows this energy to be at most -0.1 electron volt. It is therefore concluded that the segregation of iron and copper atoms with a potential energy of interaction of at least -0.7 electron volt, to which the corrosion test is sensitive, is that which occurs at sites in the core of the boundary.

One of the factors contributing to the potential energy of interaction can be estimated by calculating the lattice distortional energy, that is, the energy produced by the misfit of the solute atom in the grain-body site which is not produced when a solvent atom occupies this site. Several formulas for this calculation are given, with some revisions, by Seigle, Cohen, and Averbach (ref. 12). The distortional energy per atom of iron or copper in aluminum is a little greater than

0.1 electron volt as calculated by Lawson's formula (as revised) and about 0.5 electron volt by Scott's method (Heumann's method, also cited in ref. 12, gives negative energies at small concentrations of the smaller element). In the gold-nickel alloys studied by Seigle, Cohen, and Averbach, the distortional energies from the formula of Scott were substantially higher than the measured heats of mixing (which were believed to be due to the distortional energy) and Lawson's formula gave better agreement. The estimated distortional energy for iron or copper in aluminum is therefore taken as closer to the smaller figure. It is then concluded that the loss of grain-body distortional energy comprises only a part of the potential energy of interaction for the segregation of iron or copper and that a substantial contribution must come from a reduction in the local energy about the site in the boundary when the iron or copper atom is substituted. Although these calculations suggest that the local reduction in boundary energy accompanying the substitution of a solute atom can be quite large, from general physical considerations this would not be expected to be so large as the reduction of energy associated with the filling of a lattice vacancy. Values for the latter are thought to be in the range of 1 electron volt to 2 electron volts on the basis of calculations for copper and the alkali metals (ref. 13).

Assuming the interfacial free energy of a general grain boundary in aluminum to be roughly 500 ergs per square centimeter and to be distributed over a region about three atoms thick, the mean excess free energy per atom in the grain-boundary region is of the order of 0.1 electron volt. Then, if the segregation of iron or copper atoms at certain boundary sites is associated with a reduction in the local potential energy conservatively estimated as a few tenths of an electron volt per site, a significant reduction in the interfacial energy will not be produced unless these sites constitute an appreciable fraction of the total number in the boundary and a considerable fraction of such sites becomes occupied.

General Remarks

In the present work, it was possible to study this segregation phenomenon because special circumstances prevailed: The presence of solutes having strong segregation tendencies and thus affecting the properties of the boundaries even after quenching from elevated temperatures and when present in small amounts, a test sensitive to the concentration of solute atoms in the boundaries which was conducted at a temperature at which the boundary concentrations characteristic of different elevated temperatures could be preserved by quenching, and use of an alloy almost free of disturbing factors because of its essentially homogeneous single-phase structure where the only heterogeneities were the grain boundaries themselves. However, in view of the large interaction energies which may obtain, the possibility of considerable grain-boundary segregation is to be anticipated in most metals and alloys, especially at only slightly elevated temperatures, since impurities of substantial atomic size difference are generally present even when appreciable alloy contents are not. For example, a substantial fraction of the sites favorable for segregation will be occupied at equilibrium at 600° C with 0.01 atomic percent of a solute for which the interaction energy G at these sites is -0.7 electron volt, or with 0.5 atomic percent for -0.4 electron volt. At 200° C, equivalent boundary concentrations are attained for about 10^{-5}, 0.005, and 0.7 atomic percent of the solutes for which the respective interaction energies are -0.7, -0.4 and -0.2 electron volt. Strong segregation is favored in material treated in the lower temperature range or slowly cooled through this range even if equilibrium conditions are not attained. However, in some cases, for example, that of iron in aluminum, the extent of segregation at the lower temperatures is limited by the rapidly decreasing grain body solubility with temperature below the solvus.

While it has been concluded that grain-boundary concentrations of solute atoms are generally to be expected, there are a number of reasons why an alteration in the properties of the grain boundaries is not apparent in most metals when different solute contents or different heat-treating temperatures are compared. For one thing, the fraction of the total number of sites in the grain-boundary region which is occupied may be insufficient to modify to an observable extent any but the most sensitive properties of the boundary. Also, the changes in the properties of the boundaries may be obscured by other structural changes. For example, in corrosion the differences in solution potential which can be produced by the presence of a second phase or an attendant depleted zone, or by other concentration gradients in the matrix, are in many alloys as great as or greater than the greatest difference which has been observed between grain boundaries and bodies in a homogeneous single-phase alloy (ref. 14).

In an alloy containing sufficient solute to produce saturation of the boundaries, the addition of a second solute may produce no observable effect; further, the presence of a solute which tends to occupy a major fraction of the available sites will strongly reduce the number of sites which can be occupied by a competing solute which tends to occupy only a minor fraction of the available sites, as can be seen by inspection of equation (3). The available sites may be saturated even in a high-purity metal when strongly segregating impurities are present, as has been indicated (refs. 15 and 16) in the case of internal-friction studies of the relaxation of shear stress across the grain boundaries of aluminum alloys where the iron and copper impurities in the high-purity base material were sufficient to saturate the sites of small volume, and only with additions of an element of atomic size larger than aluminum (in this case, magnesium) could additional segregation take place and a change in the properties of the boundaries be observed. On the other hand, in the case of copper the extent of segregation in high-purity material is apparently small since a variety of alloy additions or impurities produces changes in the properties of the boundaries such as susceptibility to intergranular corrosion and stress-corrosion (ref. 17), intergranular embrittlement, or an alteration in the activation energy for recrystallization (ref. 18).

Difficulties in detecting this segregation phenomenon when comparing behavior characteristic of different equilibrium temperatures may arise if there is substantial saturation at the highest temperature used, if the interaction energy is relatively low, or if the interaction energy decreases with decreasing temperature; in any of these cases, the temperature dependence of the boundary properties may be too small to be detected. The effect of temperature is important since it permits the case in which there is actual segregation to be distinguished from the case where a substantial alloy addition affects the boundary properties without segregation, that is, even though its concentration in the boundary does not rise above the grain-body concentration; in the latter event, no temperature dependence will be observed. This distinction is inherent in certain tests which depend on the difference in properties of boundaries and bodies (e.g., intergranular corrosion) but is not made by other tests which depend only on the properties of the boundaries (e.g., internal friction). It may be noted in this connection that, for equal concentrations in the boundaries, a substantial alteration of the properties of the boundaries is more likely to occur in the case of actual segregation since then the presence of the solute atom in the boundary is associated with a reduction of the local energy.

SUMMARY OF RESULTS

The strength of the tendency for segregation to the grain boundaries of substitutional solute atoms which differ substantially in size from those of the solvent was studied in single-phase high-purity aluminum through observations on the intergranular corrosion in 20 percent hydrochloric acid. Corrosion at the general medium- and high-angle boundaries was followed, and it is to these boundaries that the results of this study apply.

1. The variation in the intergranular corrosion rate as a function of iron content and final annealing temperature was attributed to the variation of the concentrations in the grain-boundary region of the

undersize iron and possibly other impurity atoms present in the material. Precautions were taken to minimize the effects of extraneous factors on the relative intergranular corrosion rates and justification was offered for the presumption that, within the range of compositions studied, these rates were essentially functions only of the concentrations of impurity atoms in the boundaries.

2. The experimental results were analyzed by reference to a distribution function, obtained by statistical mechanical methods, which gives the equilibrium fraction of certain sites in the boundary which are occupied by solute atoms in terms of the interaction energy for the interchanging of a solvent atom at such a boundary site with a solute atom at a grain-body site. The interaction energy involves both a change in the potential energy and a change in the vibrational entropy, an estimate for the upper limit of the latter in terms of the former being obtained by the method of Zener. Application of this distribution leads to an estimate of the interaction energy but does not indicate what fraction of the total number of atomic sites in the boundary corresponds to this energy or is occupied by solute atoms under any given conditions.

3. The segregation of iron alone could not account for the observed results; from consideration of the atomic sizes and quantities of the other impurities present, it was expected that substantial segregation of copper atoms would also occur. The observed changes in intergranular corrosion rate as a function of final annealing temperature and composition could be represented as due principally to the changes in the fraction occupied by iron and copper atoms of those boundary sites where the potential energy of interaction for iron and for copper was at least as negative as -0.7 electron volt (-16,000 calories per mole) and possibly as negative as -1.0 electron volt (-23,000 calories per mole).

4. The loss of lattice distortional energy accompanying the replacement of an undersize iron or copper atom at a grain-body site by an aluminum atom was estimated and found to account only for a part of the potential energy of interaction; a substantial contribution to the latter is therefore to be attributed to a local reduction of the energy about the site in the boundary. A significant reduction of the interfacial free energy as a result of the grain-boundary segregation of these atoms is not, however, to be expected until a considerable fraction of the boundary sites of high interaction energy have become occupied.

5. It is believed that most metals and alloys contain at least one alloying element or impurity, the atoms of which have a strong

tendency to concentrate in the boundaries, but that it is only under special conditions that the effect on the properties of the boundaries can be readily detected.

Columbia University,
New York, N. Y., October 23, 1953.

APPENDIX

THERMODYNAMIC TREATMENT OF DISTRIBUTION OF SOLUTE ATOMS

The distribution of solute atoms is obtained from the thermodynamic viewpoint by considering the equilibrium state of the reaction describing the replacement of a solvent atom in the boundary by a substitutional solute atom from the grain body; that is,

$$M_2 + M_1' \rightleftarrows M_2' + M_1$$

where the subscript 1 refers to the solvent and 2 to the solute and the primed quantities indicate that the atom is at a site in the boundary. The equilibrium constant is expressed in terms of the atom fractions and the free-energy change of the reaction to give the relation

$$K = x_2'x_1/x_2x_1' = \exp\ (-\Delta F/RT)$$

and, since $x_1 = 1 - x_2 = 1 - c$, the result is

$$x_2'/(1 - x_2') = \left[c/(1 - c)\right] \exp\ (-\Delta F/RT)$$

which is equivalent to equation (1). Here the assumption made previously that strong interactions between segregated atoms do not occur becomes the assumption that the activity coefficients are the same for both grain boundary and body, that is, are independent of concentration and structure.

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TABLE I

ANALYSES OF HIGH-PURITY ALUMINUM

[Analyses furnished by the Aluminum Company of America]

Composition	Elements found, weight percent							Iron solvus temperature, °C
	Fe	Si	Cu	Mn	Mg	Na	Ca	
I	0.0004	0.0006	0.0022	<0.0002	0.0004	0.0001	<0.0002	375
II	.0039	.0007	.0022	<.0002	<.0002	.0001	<.0002	480
III	.023	.0007	.0022	<.0002	.0002	.0001	<.0002	590

TABLE II

ATOMIC DIAMETERS OF SEVERAL ELEMENTS AT ROOM TEMPERATURE

Element	Apparent atomic diameter in aluminum, kX units	Atomic diameter of element(a)
Calcium	----	3.93
Sodium	----	3.83
Magnesium	[b] [c]3.04 [d]3.11	3.19 3.20
Lithium	[b]2.82	3.13
Aluminum	----	2.86
Manganese	----	[e]2.75
Silicon	[b]2.73	[e]2.63
Copper	[b] [d]2.51	2.55
Iron	----	2.52 or 2.55

[a] Interatomic spacing in element corrected to coordination number 12.

[b] From data of Axon and Hume-Rothery, ref. 8.

[c] This value holds for less than 1 atomic percent magnesium.

[d] From data of Dorn, Pietrokowsky, and Tietz, ref. 19.

[e] There is some uncertainty in these values because of structure of elements.

TABLE III

COMPARISON FOR TWO SPECIMENS OF SUBSTANTIALLY DIFFERENT INTERGRANULAR CORROSION RATES OF FRACTION OCCUPIED BY IRON AND COPPER ATOMS OF THOSE GRAIN-BOUNDARY SITES AT WHICH INTERACTION ENERGY FOR SEGREGATION OF IRON AND OF COPPER HAS A GIVEN VALUE

[Values of $X_{Fe} + X_{Cu}$ calculated from equations (2) and (3); entropy factor has been taken as unity]

Interaction energy for iron and for copper, electron volts	-0.5	-0.6	-0.7	-0.8	-0.9	-1.0	-1.1
Fraction occupied in composition II at 647° C	0.015	0.05	0.16	0.40	0.71	0.90	0.97
Fraction occupied in composition II at 600° C	0.021	0.08	0.24	0.54	0.82	0.94	0.98

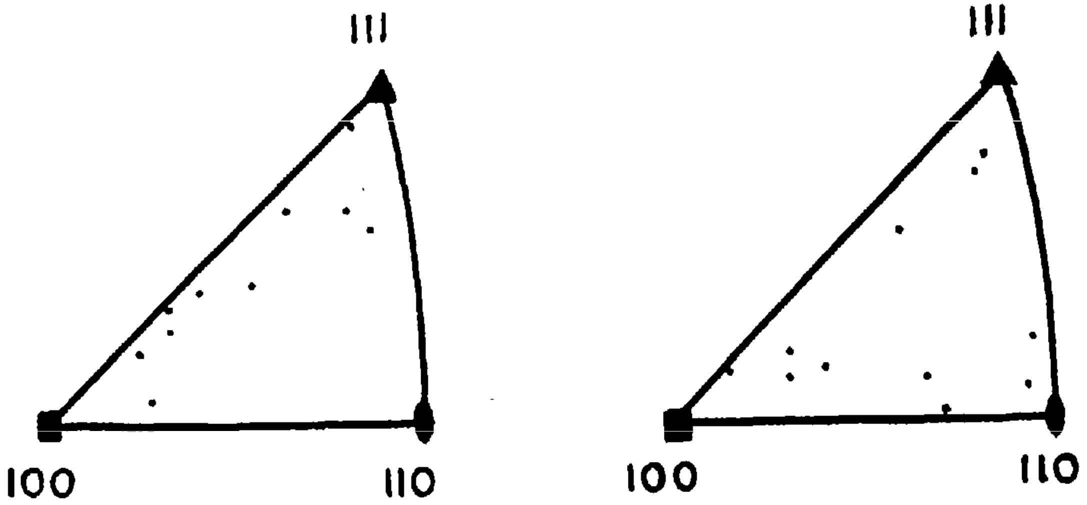
TABLE IV

COMPARISON OF RELATIVE INTERGRANULAR CORROSION RATES WITH FRACTION OCCUPIED BY IRON AND COPPER ATOMS OF THOSE GRAIN-BOUNDARY SITES AT WHICH INTERACTION ENERGY FOR SEGREGATION OF IRON AND OF COPPER IS ABOUT -0.7 ELECTRON VOLT AS CALCULATED FROM EQUATIONS (2) AND (3)

Composition (a)	Final annealing temperature, °C	Fraction of sites of assumed interaction energy occupied by iron and copper atoms, $X_{Fe} + X_{Cu}$		
		Assumed vibrational entropy factor, $\exp\left(\Delta S_v/k\right)$		
		1	0.25	0.065
		Assumed potential energy of interaction, E		
		-0.7	-0.8	-0.9
I	647	0.07	0.06	0.06
II	647	.16	.15	.13
I	575	.14	.14	.14
I	500	.27	.32	.35
II	600	.24	.23	.22
II	[b]550	.35	.36	.37
III	[b]647	.45	.42	.40

[a] In order of decreasing corrosion rate.

[b] Corrosion rates of these samples lie in a range where there may be saturation or insensitivity; if either of these is the case, equality of corrosion rates does not necessarily require equality of fractions of occupied sites.



(a) Composition I; 0.0004 percent iron.

(b) Composition III; 0.023 percent iron.

Figure 1.- Orientations of a group of grains as determined from back-reflection laue photographs. Specimens of high-purity aluminum quenched from 647° C.

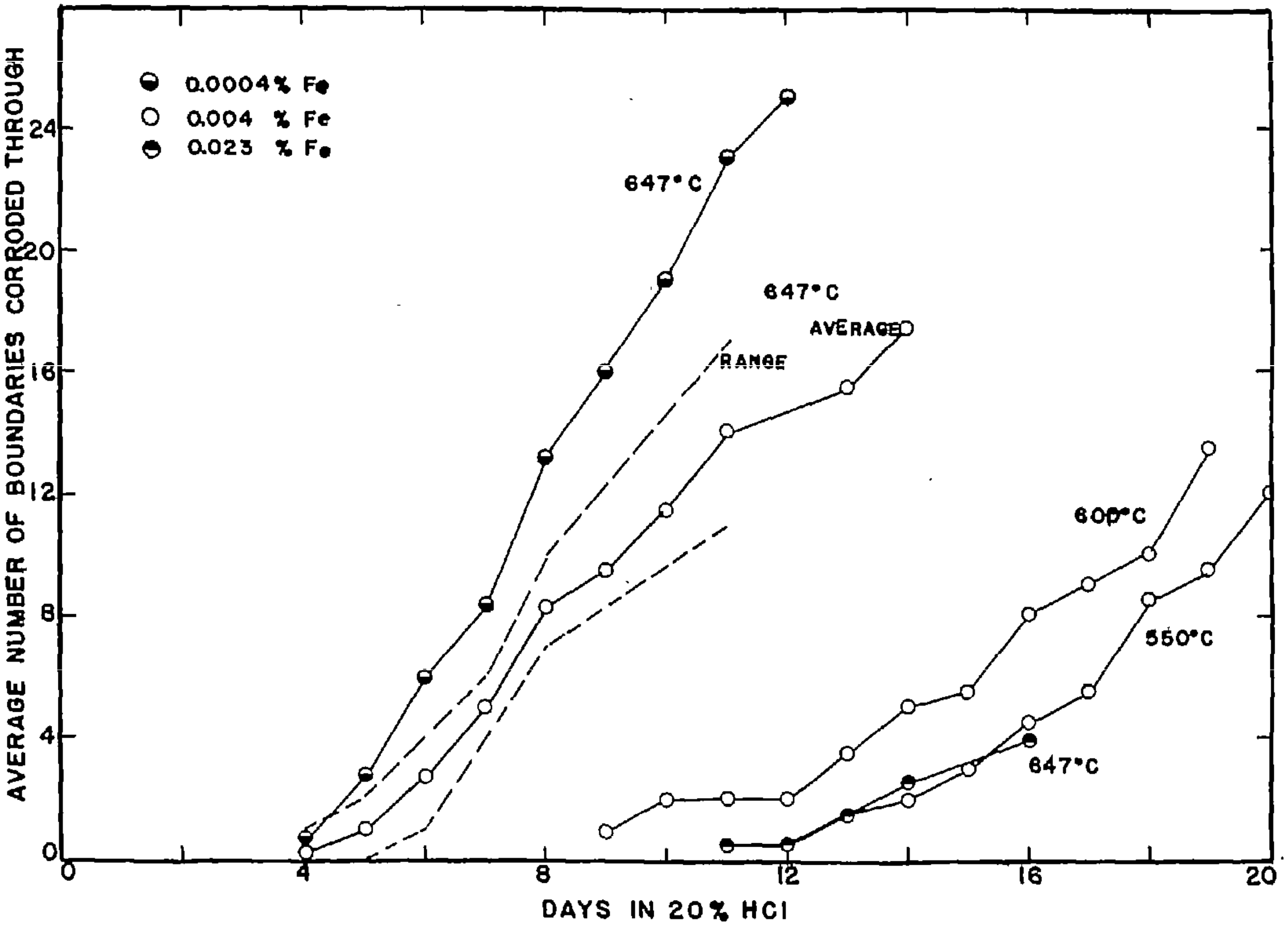


Figure 2.- Effect of iron content and final annealing temperature on rate of intergranular corrosion of high-purity aluminum containing 0.0022 percent copper. Specimens quenched from 647° C or furnace cooled from this temperature to a lower temperature, held, and quenched. Average of results of two to four tests.

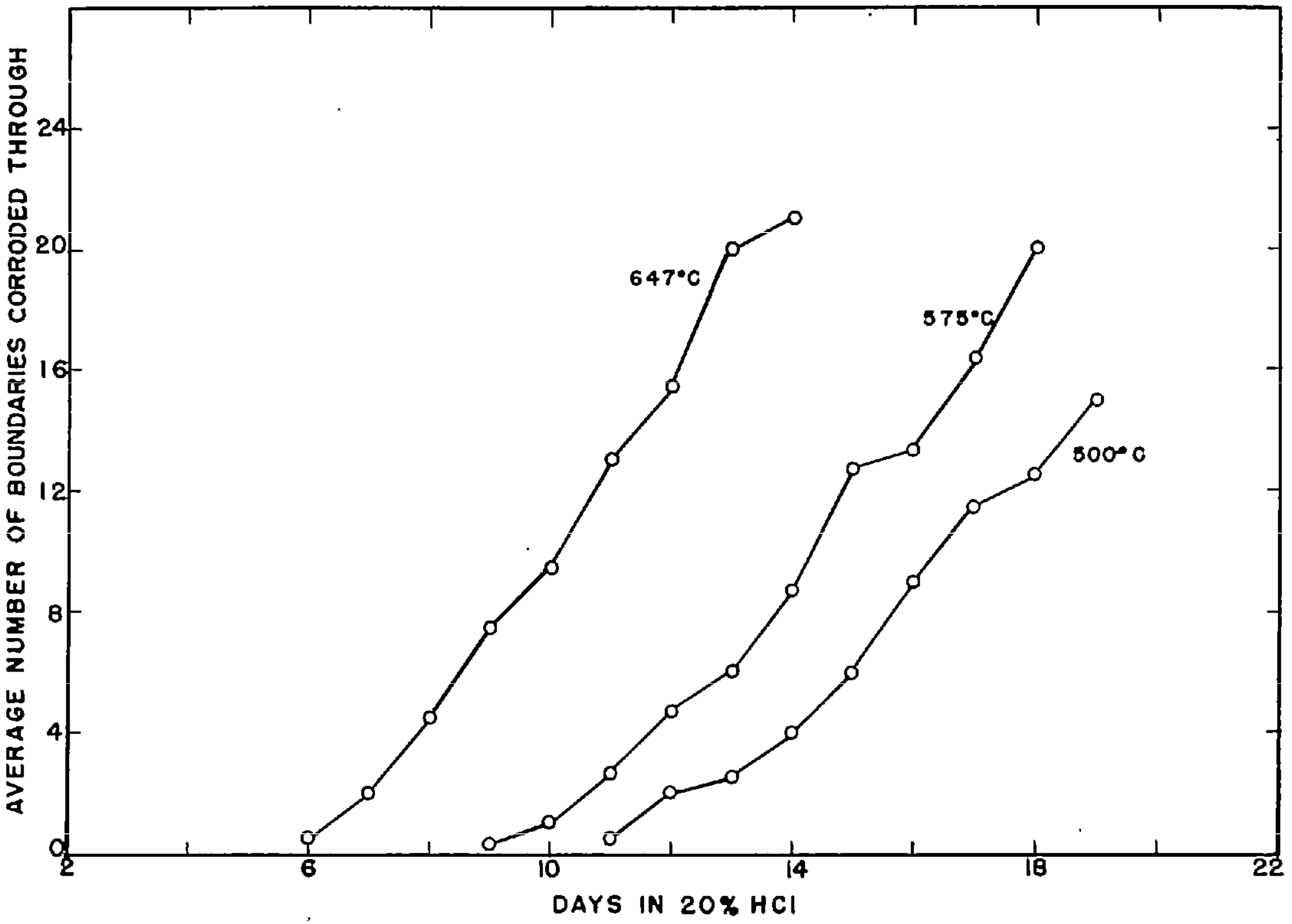


Figure 3.- Approximate effect of final annealing temperature on rate of intergranular corrosion of high-purity aluminum containing 0.0004 percent iron and 0.0022 percent copper. Samples quenched from 647° C or furnace cooled from this temperature to a lower temperature, held, and quenched. Average of two concurrent tests. Temperature of corrosion test was abnormally low from first to fourth day.

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