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A STUDY OF GRAIN BOUNDARY SEGREGATION USING THE AUGER ELECTRON EMISSION TECHNIQUE

Annual Technical Progress Report

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ABSTRACT

The influence of grain boundary chemical composition on hydrogen embrittlement was investigated. Auger electron spectroscopy was employed to determine the grain boundary compositions of nickel-copper alloys containing various concentrations of phosphorus and subjected to various thermal treatments. Phosphorus segregates to grain boundaries during slow cooling, accompanied by reduced concentrations of grain boundary copper. Tensile tests were conducted in air and following cathodic charging with hydrogen. All samples tested in air exhibited a completely ductile fracture; ductility was insensitive to grain boundary composition. Fractures of hydrogen-charged samples were brittle and intergranular; elongation to fracture increased significantly with increasing concentration of grain boundary phosphorus. The influence of phosphorus segregation on embrittlement by hydrogen or by mercury (reported previously) is analyzed in terms of additive and interactive mechanisms. A mechanism based on reduced embrittler concentration at the site of bond rupture due to improved atomic packing is proposed and found to be consistent with the experimental results of this and other investigations.

I. Introduction

The influence of grain boundary chemical composition on hydrogen embrittlement (H.E.) was determined for nickel-copper alloys. Alloy compositions correspond to Monel* 400 with various levels of added phosphorus. Previously reported work sponsored by this contract demonstrated beneficial effects of phosphorus segregated to grain boundaries in increasing the resistance of these alloys to liquid metal embrittlement (LME). Hydrogen embrittlement was employed as a means of providing intergranular fracture for grain boundary analysis in those specimens. It was noted that the segregated phosphorus had apparent effects upon hydrogen susceptibility as well and it was determined to undertake a systematic study of the phenomenon.

Hydrogen embrittlement of nickel is reported to be enabled by grain boundary antimony or tin.[1,2] Subsequent work indicates that segregated sulfur may have an important role. The embrittlement of Hastelloy C** by hydrogen has been related directly to the concentration of grain boundary phosphorus,[3] increasing P causing increased susceptibility. For nickel-copper alloys the severity of H.E. decreases with increasing copper content.[4,5]

II. Research Progress:

A. Hydrogen Embrittlement of Phosphorus-Bearing Nickel-Copper Alloys

Phosphorus Segregation Studies

Three alloys were employed; all have the composition of Monel 400, with additional phosphorus for two of the heats. Metal composition: 31 Cu, 1.3 Fe, 1.0 Mn, balance Ni, with .029 P (Alloy 1), .077 P (Alloy 2), and .159 P (Alloy 3). Specimens for scanning Auger microprobe (SAM) analysis were vacuum encapsulated in Vycor and annealed at either 900°C or 1000°C for one hour and then water quenched or furnace cooled.

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*Trademark, INCO
**Trademark, Cabot Corporation

To obtain intergranular fracture for Auger analysis, the specimens were cathodically charged with hydrogen at 1 A/cm^2, 90°C for 48 hours. These were then mounted in the SAM ultra-high vacuum system and fractured in situ. The fractures were characterized by a dominant intergranular mode.

Phosphorus was heavily enriched at the grain boundaries as shown in Fig. 1. The magnitude of the concentration varies with bulk phosphorus concentration, annealing temperature and cooling rate. Increasing phosphorus at the boundary is accompanied by decreasing copper as shown in Fig. 2. Guttman's[6] treatment of segregation in ternary alloys predicts that solute elements interacting more weakly with the segregant than the solvent will tend to be depleted at the boundary. The heat of formation of Cu_3P is -30,800 cal/mol while that of Ni_3P is -47,800 cal/mol. Accordingly, Guttman's analysis predicts the copper depletion observed in the present study.

Analysis of the depth profiles of phosphorus, obtained by Argon sputtering, yielded steep gradients of segregant which were shown to be consistent with a process of equilibrium segregation.

B. Hydrogen Embrittlement Measurements

Base line data for structure and tensile properties were established. It was determined that although the concentration of grain boundary phosphorus varied greatly for the several compositions and heat treatments employed, the tensile properties measured in air did not significantly change. All specimens elongated about 55% in 1.0 cm and fractured in a ductile manner. The grain size for all alloys and heat treatments was measured by the linear intercept method.

Hydrogen embrittlement testing was performed on Alloy 1 quenched and furnace cooled from 900°C and on Alloy 2 quenched from 900°C. Tensile samples were then prepared. All areas of the sample except the gage section were coated with lacquer. Samples were cathodically charged using a platinum wire anode

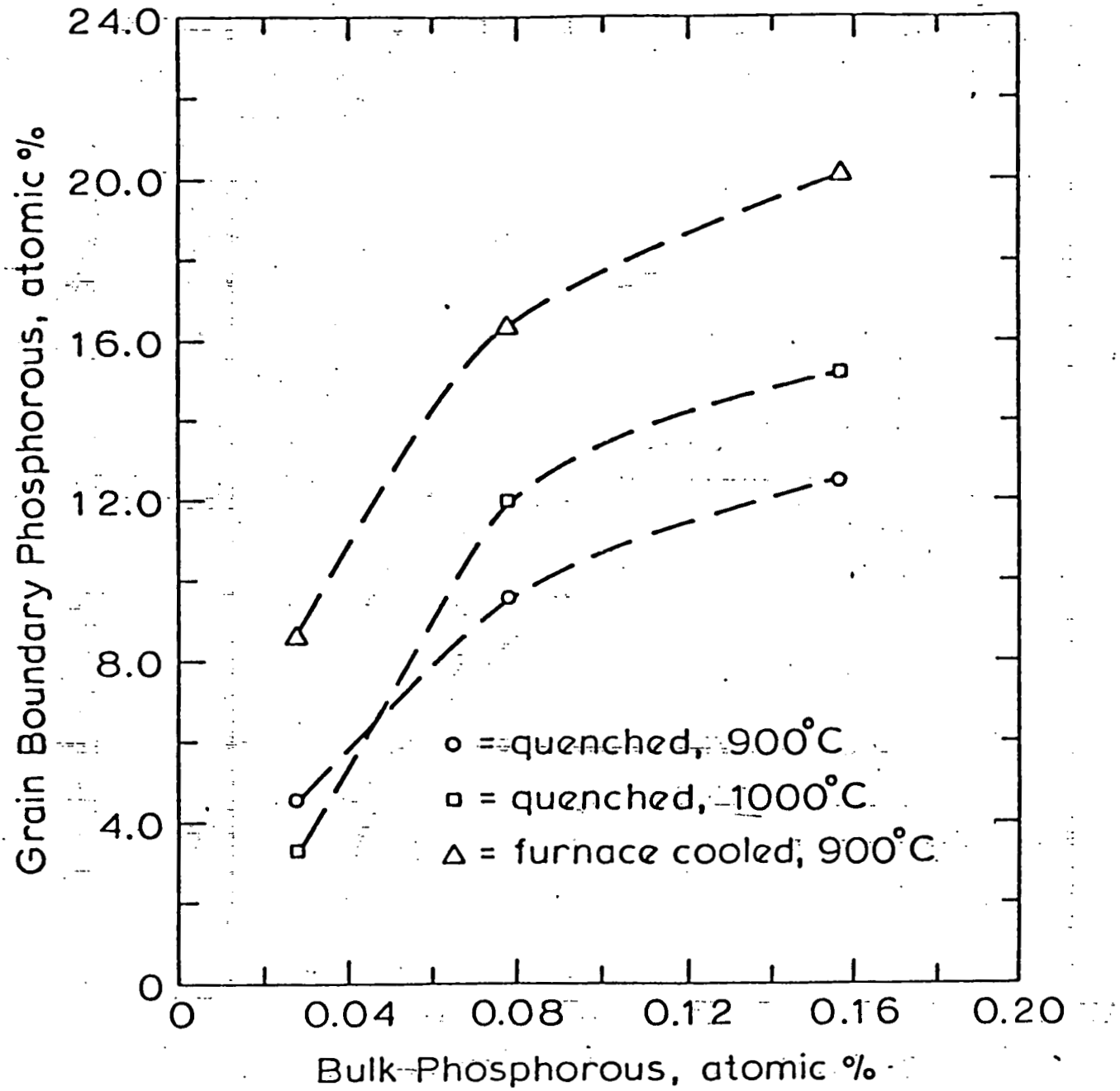


Figure 1. - Grain boundary phosphorus concentration versus bulk phosphorus concentration.

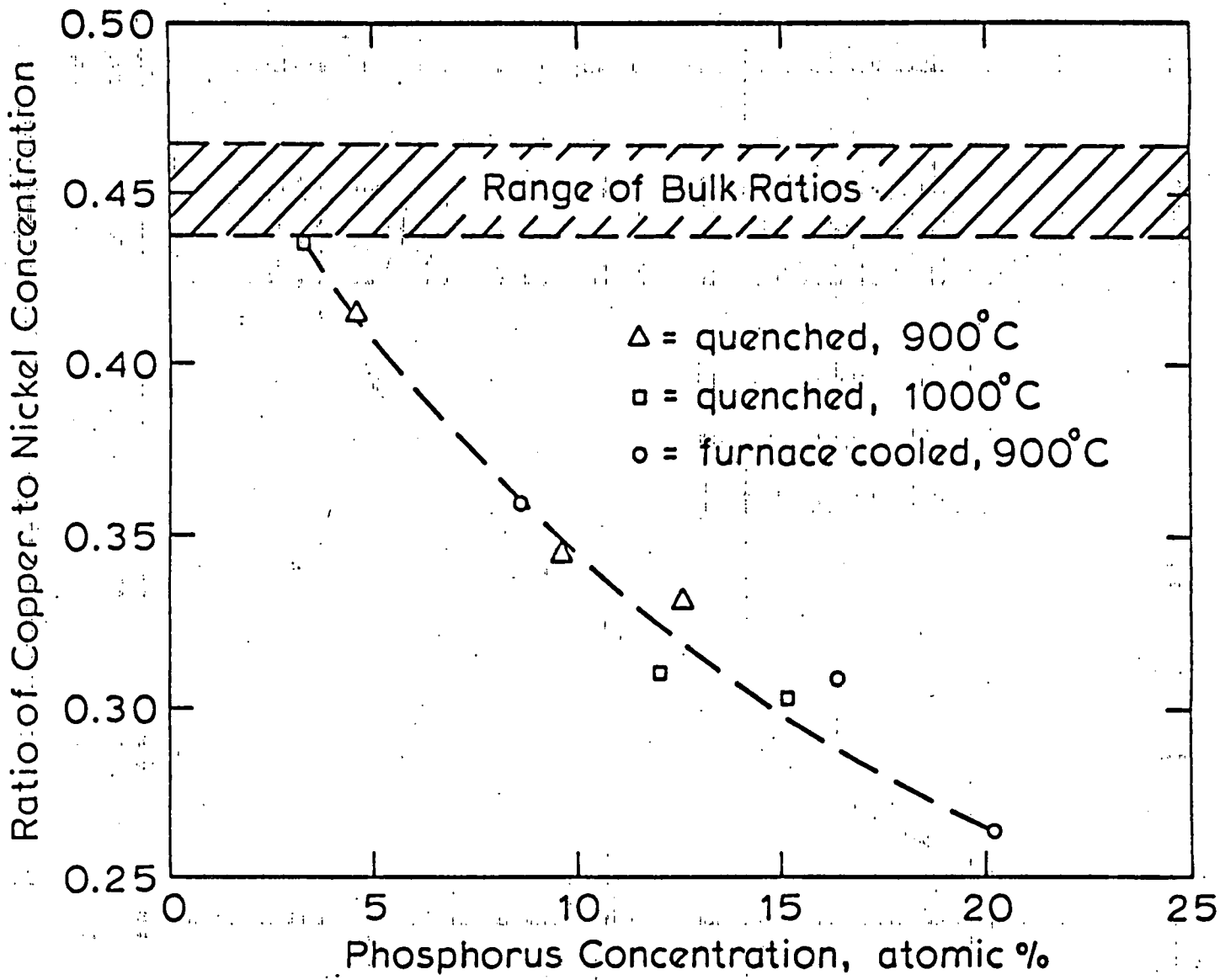


Figure 2. - Ratio of copper to nickel concentration versus grain boundary phosphorus concentration.

and a solution of 5% H_2SO_4 with 0.25g/l of sodium arsenite added to poison hydrogen recombination. Charging was continued for 100 hrs. at 90°C using current densities of either 10, 14, or 20 ma/cm^2. Samples of Alloy 2 were charged at 10 ma/cm^2 only. The hydrogen concentration in the center of the samples was estimated to be 87% of the surface concentration. The diffusivity of hydrogen was assumed to be 10^{-8} cm^2/sec since this value is characteristic of both nickel and copper at 90°C.[7]

Following charging, samples were polished with 600 grit SiC paper and inspected to insure that no surface cracks were present. Tensile tests were conducted at a crosshead rate of 0.0127 cm/min. (nominal strain = 0.13 min.$^{-1}$), and load-time curves were converted to engineering stress-strain curves. Hydrogen charging reduced material ductility by promoting sudden brittle fracture but did not alter material flow detectably prior to fracture. Average fracture stresses and elongations are presented in Table I.

By optical microscopy, it was determined that all samples contained cracks which had not participated in sample fracture. SEM fractography revealed that samples had failed predominantly by intergranular separation with isolated areas of transgranular fracture as observed in Fig. 3. The area occupied by transgranular fracture increased with increasing fracture stress.

C. Discussion

The observed intergranular fracture mode is characteristic of hydrogen embrittlement of nickel and nickel-base alloys. Intergranular fracture can be attributed to the intrinsic weakness of grain boundaries relative to other surfaces. Hydrogen segregation to grain boundaries due to its low matrix solubility probably also contributes to intergranular fracture.

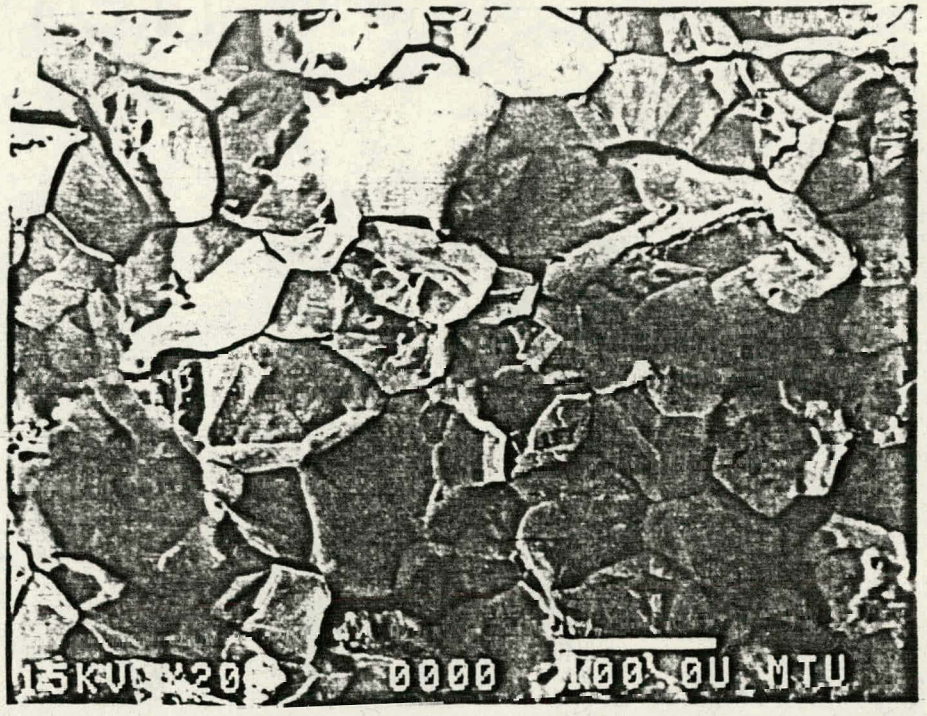
The isolated areas of transgranular fracture had a definite crystallographic nature which indicated that fracture was not merely the result of ductile tearing to connect areas of grain boundary fracture. Crack growth had definitely

Table I

Average Tensile Properties after Cathodic Charging

Alloy	Condition	I., MA/CM^2	F.S., MPa	El., %	El., % (no hydrogen)
1	Q., 900°C	10	392	23	56
2	Q., 900°C	10	478	34	54
1	F.C., 900°C	10	512	35	54
1	Q., 900°C	14	299	7	56
1	F.C., 900°C	14	390	13	54
1*	Q., 900°C	20	249	5	56
1*	F.C., 900°C	20	302	8	54

Q. = Quenched
F.C. = Furnace Cooled
I. = Current Density
F.S. = Fracture Stress
El. = Total Elongation in 0.94 cm
* = Average of 4 tests, all others 2 tests



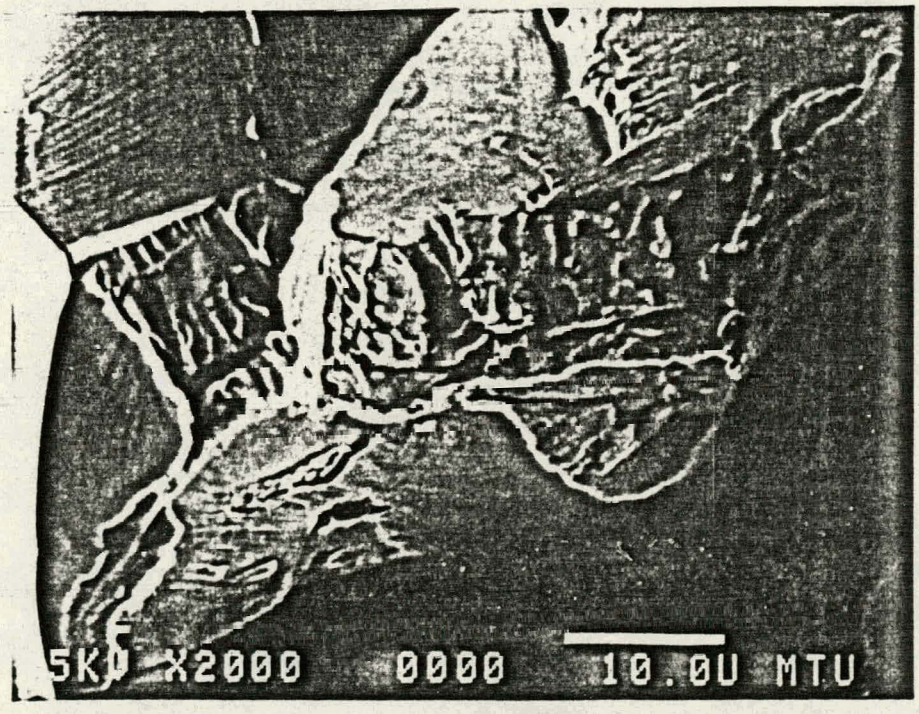


Figure 3 - SEM fractographs of alloy 1 quenched from 900°C and hydrogen charged at 10 ma/cm^2.

been affected by the presence of hydrogen. The fracture mode was not totally cleavage as indicated by the lack of characteristic river patterns and flat plateaus. It is probable that fracture was a result of quasicleavage which combined ductile tearing and cleavage.

Fracture stress and elongation are shown as a function of charging current density in Figs. 4 and 5. Increased current density reduced fracture stress and elongation and reduced the areas of transgranular fracture observed on fracture surfaces. This is attributable to the higher hydrogen concentrations present in samples charged at higher current densities. The hydrogen concentration of all samples was definitely less than the 0.2 atomic % which is present in pure nickel after charging at 50 ma/cm^2.[4]

Material susceptibility to H.E. was reduced by increased grain boundary phosphorus concentration. Furnace cooled Alloy 1 (8.6% phosphorus) had higher fracture stresses and elongations than quenched Alloy 1 (4.6% phosphorus) for all charging current densities (Figs. 4 and 5). No differences existed in microstructure which could account for this difference. The fact that quenched Alloy 2 and furnace cooled Alloy 1 had similar grain boundary chemical compositions and tensile properties after hydrogen charging (Table I) further indicates that embrittlement severity is controlled by grain boundary phosphorus concentration.

These results may be considered in terms of various proposed hydrogen embrittlement mechanisms. Both pores, indicative of an internal pressure mechanism, and topographical features, indicative of the presence of hydrides, were absent on the fracture surfaces. The fact that the current densities employed for hydrogen charging were well below those required for surface hydride formation on nickel[4] further reduces the likelihood that a hydride embrittlement mechanism was operating. Embrittlement due to a restriction of dislocation motion is unlikely since yield and flow stress were not affected by hydrogen

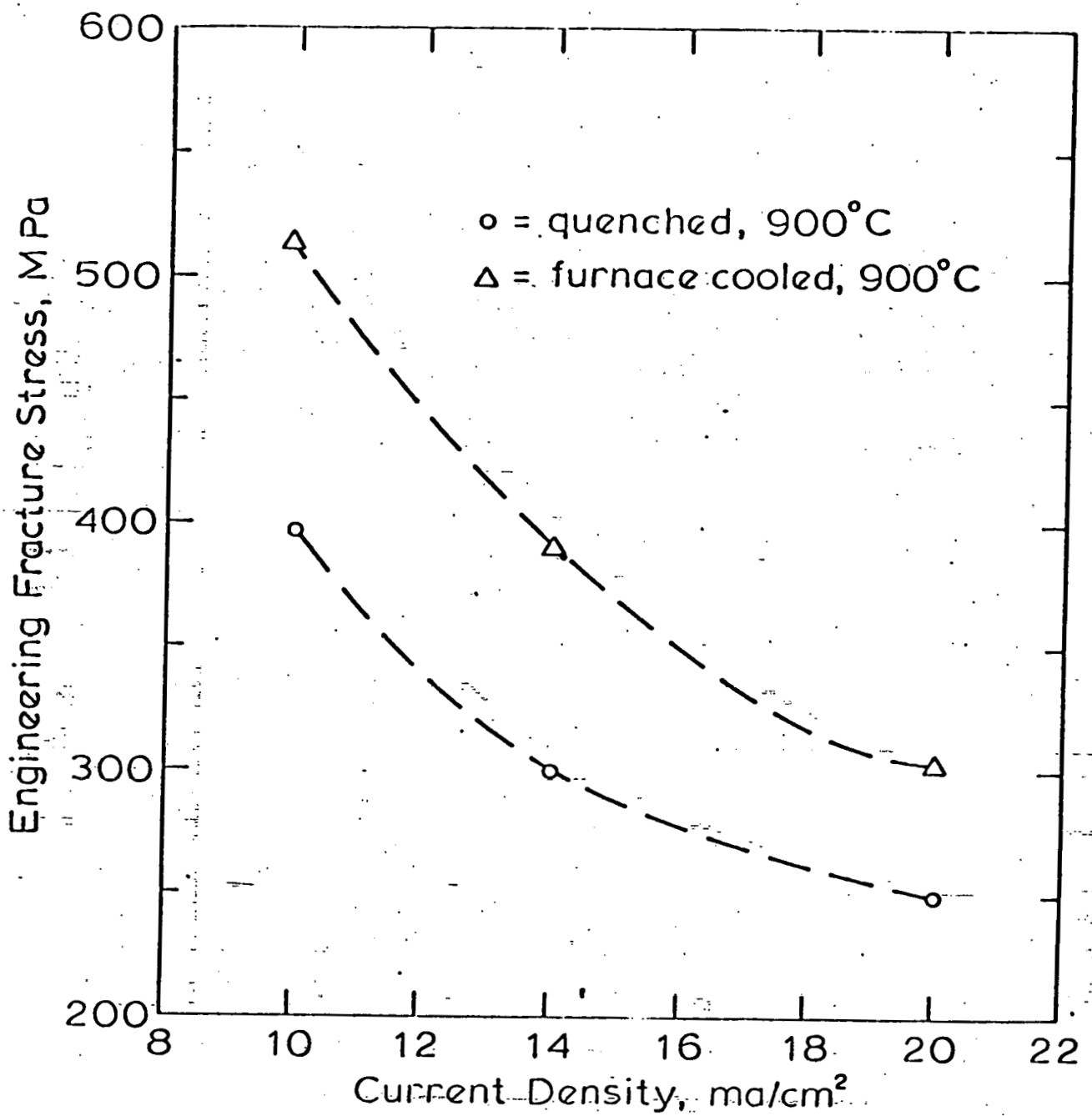


Figure 4. - Engineering fracture stress versus charging current density.

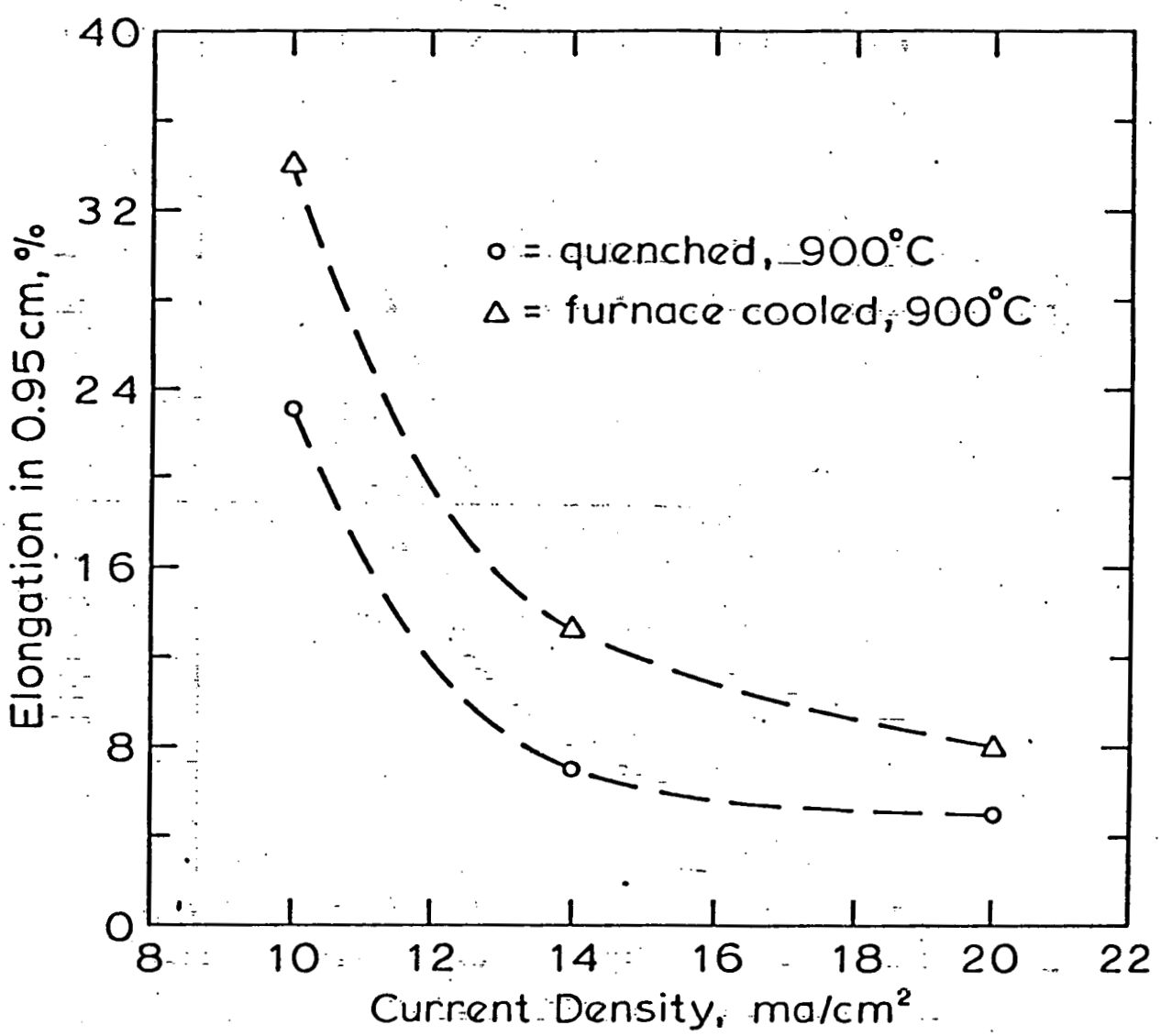


Figure 5. - Elongation in 0.95 cm versus current density for alloy 1 quenched and furnace cooled from 900°C

charging. Embrittlement by enhanced dislocation nucleation and movement on slip planes intersecting the crack tip (crack growth by alternate shear) is not supported by the smooth appearance of the grain boundary fracture surfaces. This mechanism is also contradicted by studies which show that dislocation motion in nickel is actually impeded by hydrogen at low temperatures or low strain rates.[4]

Only the lattice decohesion mechanism is capable of producing the smooth intergranular fracture surfaces which were observed without significantly influencing material flow. This mechanism involves reduced energy required to create new surfaces due to reduced bond strength.[8,9] The precise mechanism by which hydrogen, or liquid metals, act to reduce bond strength in materials has not been identified. Prior to testing, it is likely that hydrogen will be segregated to grain boundaries. During testing, hydrogen's mobility will allow it to move to sites of high stress concentration which includes blocked slip bands and the crack tip region. Therefore, hydrogen may be further concentrated in those areas where it promotes crack nucleation and propagation.

D. Mechanism of Phosphorus Effects

As reported here and in the previous Technical Progress Report, it has been found that increased grain boundary phosphorus concentrations reduces the embrittlement of Monel by both hydrogen and mercury. It is remarkable that embrittlement by two very different embrittler species would have an identical response to changes in grain boundary composition. Mercury is a large metallic atom which does not penetrate the material lattice, while hydrogen is a small interstitial solute.

The objective of this section is to analyze these results in order to obtain an understanding of the influence of grain boundary composition on LME and H.E. It will be assumed that embrittlement is caused by reduced atomic cohesion. Both additive and interactive roles for phosphorus will be considered.

An additive role implies that phosphorus exerts its own positive influence on atomic cohesion which counters the negative influence of hydrogen and mercury. An interactive role indicates that phosphorus acts to reduce the effectiveness of the embrittlers.

1. Additive Influence

The absence of intergranular fracture for materials tested in air prevents an experimental determination of the influence of phosphorus segregation on atomic cohesion along grain boundaries in the absence of mercury or hydrogen. However, large decreases in cohesion due to increased phosphorus concentration can be ruled out since intergranular fracture was not observed with phosphorus concentrations as high as 20 atomic percent.

Seah has postulated that, based upon some observations in steels, segregants having smaller atomic size than iron improve strength by increasing the atomic density along boundaries; conversely, large segregants reduce strength by the same reasoning. There are reservations about the above hypothesis because of several observed exceptions and also because interactive mechanisms can explain these effects in certain cases. Regardless, phosphorus has a larger size than either copper or nickel and thus would not have a strengthening effect according to the Seah hypothesis.

2. Interactive Influence

Segregants may interact chemically with an embrittling species to influence its concentration and embrittlement severity. If the chemical bonds between the segregant and the embrittler are stronger than those between the solvent and the embrittler, increased embrittler adsorption and embrittlement is predicted. On the other hand, if the chemical bonds between the segregant and the embrittler are relatively weak, reduced embrittler adsorption and embrittlement should take place. While this bond strength approach to chemical interaction is rudimentary, it is consistent with the solution used successfully

by Guttman[6] to treat cosegregation and demixing in ternary alloys.

Since phosphorus replaces copper at grain boundaries in Monel, the relative bond strengths between these elements and mercury and hydrogen are of interest. Mercury and copper interact to form intermetallic compounds while no reaction occurs between mercury and phosphorus.[10] Therefore, reduced mercury embrittlement due to phosphorus segregation may be rationalized in terms of reduced mercury-adsorption. However, phosphorus segregation would not be predicted to reduce hydrogen embrittlement based upon chemical interactions. The diatomic bond strength between hydrogen and phosphorus is 82 kcal/mole while between copper and hydrogen it is 67 kcal/mole.[11]

3. Physical Interaction

A grain boundary can be considered to be a thin region of material which separates two crystals of different orientation and which is disordered in the sense that nearest neighbor relationships and interatomic distances are altered.[12] In some locations interatomic distances are too large while in other locations they are too small. In pure materials grain boundary energy is a measure of this disorder. For impure materials, grain boundary energy is also dependent on chemical composition.

It is the disordered nature of the grain boundary which makes it an attractive location for solutes which do not fit well into the lattice due to atomic size or electronic differences with the solvent. When a solute moves to the grain boundary, the properties of the grain boundary are affected. Experiments have demonstrated that grain boundary energy is reduced by segregation.[13]

A portion of the decrease in grain boundary energy accompanying solute segregation is due to the better atomic packing density which can be attained along the grain boundary when atoms of different atomic size are present.[14] For example, copper and gold are both elements of group I in the periodic table which exhibit the same valence electron configuration, have fcc crystal structures, and form a

continuous series of solid solutions. However, gold's atomic diameter (2.88Å) is significantly larger than copper's (2.56Å). A decrease in grain boundary energy accompanies both gold additions to copper and copper additions to gold.[15] Since gold and copper are similar electronically, this change in grain boundary energy can be attributed principally to better atomic packing along grain boundaries when atoms of two different atomic sizes are present. It is important to note that atomic packing can be improved by additions of both large and small solute atoms.

Based upon the preceding discussion, segregation of phosphorus in Monel would be anticipated to improve atomic packing along grain boundaries. The atomic diameter of phosphorus in metallic solution is 2.72Å[16] while that of copper and nickel are 2.56Å and 2.49Å. The influence of this improved packing on mercury and liquid metal embrittlement must be considered.

Hydrogen has a very low solubility in nickel alloys and expands the nickel lattice.[17] Hydrogen segregation to regions of disorder such as grain boundaries would be expected. Improvement in atomic packing along the grain boundary due to phosphorus segregation should reduce hydrogen concentration at grain boundaries thereby reducing hydrogen embrittlement.

Mercury is a large atom (3.01Å), the adsorption of which would be facilitated at regions of high atomic disorder and poor atomic packing. Therefore, reduced mercury adsorption and reduced embrittlement due to phosphorus segregation to grain boundaries can also be attributed to physical interactions.

Dinda[18] has also suggested that phosphorus' role in reducing lead and tin embrittlement of steel can be attributed to improved atomic packing along grain boundaries. In this case, phosphorus' atomic size is smaller than that of iron. Dinda incorrectly suggests that the segregation of atoms larger than iron will reduce atomic packing efficiencies and thereby increase embrittlement.

4. Summary

The preceding analysis suggests that the beneficial influence of phosphorus can be attributed to: (1) an absence of significant reductions in grain boundary cohesion due to phosphorus segregation and (2) reduced adsorption of both mercury and hydrogen at the grain boundary due to increased atomic packing density. Hypothesis 2 finds considerable support in studies of the influence of grain boundary orientation on H.E. and LME of pure materials:

Kargol[19] determined the influence of tilt boundary energy on the liquid metal embrittlement of 99.993% pure aluminum bicrystals in Hg-3% Ga. Crack extension force and boundary energy were measured as a function of tilt angle. Decreased boundary energy (improved atomic packing along boundaries) was seen to increase the crack extension force (reduce embrittlement).

Rath[20] studied the influence of grain boundary energy on the incidence of cracking induced by cathodic charging of purified iron. It was observed that the incidence of cracking increased with angular misorientation across the boundary. The results were rationalized in terms of atomic misfit in the boundaries. Boundaries of low atomic misfit (high atomic packing density) are more resistant to cracking.

III. Publications and Presentations Associated with Contract

A. Publications

1. "Grain Boundary Segregation and Materials Properties," D. F. Stein and L. A. Heldt, in Grain Boundary Segregation, American Society for Metals, 1979.

2. "A Study of Intergranular Fracture in Cu-Sb Alloys Exposed to Acid Sulfate Solution," T. R. Pinchback and L. A. Heldt, in Environment-Sensitive Fracture of Engineering Materials, TMS-AIME, 1979.

3. "Grain Boundary Segregation: Effects on Stress Corrosion and Liquid Metal Embrittlement," L. A. Heldt, A. W. Funkenbusch, D. F. Stein and T. R. Pinchback, Corrosion 79, NACE, 1979.

4. "Grain Boundary Segregation of Sulfur in Molybdenum," S. M. Tuominen and S. P. Clough, Met. Trans., 10A, 127 (1979).

B. Invited Presentations

1. "Grain Boundary Segregation: Effects on Stress Corrosion and Liquid Metal Embrittlement," L. A. Heldt, A. W. Funkenbusch, D. F. Stein, and T. R. Pinchback, Symposium on Alloy Composition and the Nature of Corrosion Films, NACE, Atlanta, GA., March, 1979.

2. "Embrittlement of Nickel-Copper by Hydrogen and by Mercury: Influence of Grain Boundary Chemistry," A. W. Funkenbusch, L. A. Heldt, and D. F. Stein, Symposium on Analytical Techniques for Corrosion, TMS-AIME, Milwaukee, WI., September, 1979.

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