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STRESS CORROSION CRACKING CONTROL PLANS. 3. COPPER ALLOYS

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3. Copper Alloys

Note: Subject to revision. The author would appreciate suggestions.

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COPPER ALLOYS

ALLOY NOMENCLATURE

The atomic arrangement in crystals of pure copper is face-centered cubic, and as long as this arrangement is retained in copper alloys, they are designated alpha alloys, such as alpha brass. If a brass contains more than about 35% zinc, grains of a second phase termed beta appear among the alpha grains. The beta phase has the atoms arranged in a body-centered cubic lattice. Brasses containing both phases are termed alpha-beta brasses. Above about 40% zinc the alloys consist of all beta grains and are termed beta brasses. Beta brass alloys are rare in commerce, but a few are produced in Europe.

Copper alloys are not strengthened by heat treatment, with few exceptions, notably beryllium copper. But they are commonly strengthened by cold working.

The term bronze was once reserved for copper alloys in which the principal alloy addition was tin, but the term has been debased to the point that its use serves little more than to exclude the nearly all-copper alloys and the nearly pure binary copper-zinc alloys (brasses).

AMMONIACAL SCC

A principal environment causing SCC in copper alloys, although not the only one, is generally believed to involve ammoniacal compounds. SCC in the copper/ammoniacal system has often been termed "season cracking" by leading authorities, but there is a lack of unanimity in defining this term by various authors and nomenclature committees. Therefore to avoid any possible confusion the term "ammoniacal SCC" will be used here instead, though even so it should be understood that the word "ammoniacal" is a convenience intended to include amines and all other species which can react with copper to produce the cupric-ammonium complex ion or perhaps structurally similar complexes.

If one learns how to avoid ammoniacal SCC, a large proportion of the practical SCC threat to copper alloys will have been prevented. Not only is it considered a principal SCC hazard to copper alloys, but it is also the SCC system for which we have the most intercomparable laboratory data and field experience by far. We will therefore treat ammoniacal SCC as the principal topic of this chapter, thereafter treating the other alloy/environment systems which do not fit into the major group. These other systems, though they have been responsible historically for fewer SCC failures than ammoniacal SCC, can nevertheless be extremely troublesome, as will be seen. It should be especially noted that recent studies with copper sulfate and copper nitrate solutions suggest that some of the service failures surmised to have been caused by ammonia may have been caused rather by sulfate or nitrate ions in stagnant aqueous situations on copper alloys under conditions permitting the generations of concentrated copper solutions. Also some of the SCC failures occurring in the atmosphere and attributed to ammonia may have been caused instead by sulfur dioxide, oxides of nitrogen, or other contaminants, as discussed under "SCC IN OTHER ENVIRONMENTS" below.

Necessary Conditions

There are five conditions which must be met before ammoniacal SCC occurs:

1. Water
2. Oxygen
3. Tensile stress
4. Alloy of susceptible composition and structure
5. Ammonia

Considering these in turn,

(1) Water must be present, probably in the condensed liquid state; a film of moisture on the metal surface suffices to cause cracking if other conditions are met. It appears possible that there are hygroscopic corrosion products which can produce the aqueous film believed necessary in an atmosphere well above the dew point. An

example of cracking attributed to the action of deliquescent contaminants and another example attributed to a film of condensate caused by dew-point conditions will be described.

(2) Oxygen or an oxidizing agent must be present, unless there is an independent source of copper ions in solution. An example will be given illustrating how preventing access of oxygen is a practical strategy to avoid ammoniacal SCC in some situations. The higher the oxygen content of the environment the higher is the incidence of SCC (other necessary factors being supplied and kept constant), but quantitative data are lacking.

As a corollary of (1) and (2), anhydrous ammonia having neither water nor oxygen is quite compatible with copper alloys, even those which are highly susceptible to ammoniacal SCC.

(3) Tensile stress must be present, and the hazardous level may vary from a small fraction of the yield strength depending upon the alloy and the environment. This stress may be supplied by working stress (design stress), assembly stress, cold work remaining from forming operations, or any combination of these stresses as long as their vector sum on the surface is a tensile stress of sufficient magnitude. In structures or components likely to be made of copper alloys it is seldom the design stresses which are important to cracking, but rather the stresses residual from cold forming (as by spinning, drawing, sinking, roll-forming,

stamping) or fit up or assembly stresses, including especially straightening or bending of pipe or tubing. As a corollary of this generalization, thickening the structural elements is seldom effective in avoiding the cracking problem in the applications for which these alloys are commonly used. As another corollary, since castings are usually much freer from residual stresses than unannealed wrought products, they are not nearly as frequently beset by the cracking problem as wrought products. Two apparently similar forming methods to produce the same product may generate vastly different residual stresses. For example forming tubing by pulling it through a die without internal support ("sinking") leaves vastly higher residual stresses than pulling over an internal support or mandril ("drawing").

One way to remove the hazard of SCC caused by cold work is to anneal the product, but the reader is warned that removing the cold work by annealing is no guarantee that stresses of hazardous magnitude may not be re-introduced by even minor subsequent deformation, even dropping the annealed article from the bench to the floor!

If one decides the tactic to be used to avoid SCC in a given product includes removal of cold-work stresses, he may elect to specify either a full (recrystallization) anneal or alternatively a stress-relief anneal. Achievement of full annealing can be verified by hardness measurements of (if feasible) by metallographic examination, of if the produce is one whose recrystallization characteristics are well known as for example brass condenser tubes, one may rely upon a conservative specification based on experience. If however one does not wish to sacrifice strength and anneal only enough for stress relief, experimentation may be needed. Table I gives some guidance for such stress relief treatments and illustrates the wide

TABLE I

Typical stress relief annealing temperatures*

Alloy name	Alloy number**	Temperature***	
Commercial bronze	C 220 00	400°F	204°C
Cartride brass	C 260 00	500	260
Muntz metal	C 280 00	375	190
Admiralty brass	C 443 00	575	302
Cupronickel (30%)	C 715 00	800	426
Phosphor bronze (5%)	C 510 00	375	190
Phosphor bronze (10%)	C 524 00	375	190
Silicon bronze (3%)	C 655 00	700	371
Aluminum bronze D	C 614 00	1112	600

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*After Metals Handbook, 8th ed., vol. 1, p. 1001, ASM, Metals Park, OH, 1961.

**ASTM-SAE Unified Numbering System for Metals and Alloys. The first three digits are the Copper Development Association designations for the same alloys.

***Suggested annealing time for Muntz metal is 1/2-hour; for all other alloys listed, 1 hour.

range of annealing temperatures which may be required. The temperatures in Table I are typical values only. If for a given cold-worked product avoiding SCC depends critically on relief of cold-work stresses, the exact minimum annealing temperatures must be found by trial, as it varies with such factors as composition, degree of cold work, and microstructure. The procedure then is to try some annealing temperature near the typical ones shown, afterward exposing the heat treated article to see whether it will crack in the most hazardous environment (from the point of view of SCC) to be encountered in service, if this most hazardous environment is known, which is uncommon. If it is not known then an arbitrary severe standard test environment may be used.

There is a quick test which is used to detect high and even moderate stresses in many copper alloys, employing acidified mercurous nitrate as the environment. This test has been standardized as ASTM B154-71. In this test the article is acid-pickled to remove oxides, rinsed in running water, immersed for 30 minutes in an aqueous solution of 10g $Hg_2(NO_3)_2$ (11.4 g if tetrahydrate) plus 10 ml concentrated HNO_3 per liter, and examined for cracks. Note that this is not necessarily a test for susceptibility to SCC but rather a qualitative and potentially destructive test for residual stresses in copper alloys.

The mercurous nitrate environment acts more rapidly than ammoniacal environments; but at low stresses the mercurous nitrate may not crack an article which cracks (albeit slowly) in a concentrated ammonia environment. Thus passing the mercurous nitrate test is no guarantee against subsequent failure in an ammoniacal environment.

But note that some alloys (C 619 00, C 638 00, and C 688 00) may, when annealed in certain temperature ranges, undergo an ordering reaction which may increase the degree of susceptibility to ammoniacal SCC even though partial stress-relief has occurred. Hence the mercurous nitrate test, which checks only for residual stress, not susceptibility, is not as conservative a test for these alloys as an ammoniacal test.

Note also that an article such as a condenser tube may be adequately annealed or stress relieved only to have stresses of dangerous level re-introduced by straightening, denting, cutting and deburring, or improper installation. For these reason conservative practice does not rely solely on annealing to avoid SCC.

Unfortunately to verify adequate annealing for stress relief only there is no practical alternative to potentially destructive tests, though one may elect to over-anneal and thereby soften the alloy enough that hardness or microstructure can be used as evidence of the stress relief. Conservative practice limits straightening brass tubing after final annealing to 2-plane straightening and disallows rotary straightening.

(4) An <u>alloy of susceptible composition and structure</u> is a fourth (and obvious) condition which must be met before ammoniacal SCC is a problem; the degree of susceptibility differs enormously among copper alloys. One measure of degree of susceptiblity is the highest stress which the alloy will sustain in a specified environment without cracking. Data of this sort from a "season cracker" environment are shown in Table II for various alloys in assorted degrees of cold work. The experiments from which this table was constructed extended to about 1,000 hrs., which appears adequate to characterize a threshold stress for this system. It would be very unwise to use the stresses in Table II as design working stresses for critical parts, but when considered together with other data and experience these stress levels provide the basis for the very useful general classification of the relative resistance of various classes of copper alloys to season cracking shown in Table III. The purist might wish for a more quantitative presentation than is shown in Table III, but the data are simply not available for it, nor is it certain that the quantification would be interpretable in practice since in many applications we do not know either the stress in the completed and operating structure or the environment very well. Minor

TABLE II

Approximate sustained tensile stress for several copper alloys in an atmosphere of 16% NH_3, 4% H_2O, balance air, at 35°C.*

Alloy name	Alloy number	Temper	Stress***	
			ksi	MNm^{-2}
Cu-30% Ni	C 715 00	70% reduction	85	585
Silnic bronze	C 747 00	75% reduction, aged	80	550
Cu-30% Ni	C 715 00	annealed	60	410
High silicon bronze	C 655 00	6 hard**	50	345
Commercial bronze (10% Zn)	C 220 00	4 hard	40	275
Electrolytic tough pitch copper	C 110 00	annealed	35	240
Low brass (20% Zn)	C 240 00	4 hard	35	240
Silnic bronze	C 647 00	solution treated, aged	20	140
High silicon bronze	C 655 00	annealed	20	140
Admiralty brass	--	annealed	10	70
Commercial bronze (10% Zn)	C 220 00	annealed	10	70
Low brass (20% Zn)	C 240 00	annealed	10	70
Antimonial Admiralty brass	C 444 00	2 hard or annealed	5	35
Low silicon bronze	C 651 00	annealed	5	35
Cartridge brass	C 260 00	annealed or cold worked	less than 5	<35
Muntz metal	C 280 00	annealed or cold worked	less than 5	<35
Admiralty brass	--	6 hard	less than 5	<35

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*After Whittaker (1), quoting data of Thompson and Tracy (2).

"6 hard" etc.: An arbitrary copper industry scale of hardness due to cold work **ranging from 1 hard (approx. Rockwell B68) to 8 hard (about B 97).

***These stresses are not to be used in design. See text.

impurities in a highly susceptible alloy such as cartridge brass (30% Zn) have not been found to affect susceptibility. But note in Table III that the small amount of P in phosphorized copper causes this alloy to be in a distinctly more susceptible category than the phosphorus-free tough pitch copper.

Other alloys have been reported susceptible to ammoniacal SCC, but the data are not easily compared with those from which Table III was made. These miscellaneous alloys are Cu-Si-Mn; Cu-Au; Cu-Si; Cu-Ni-Si; Cu-Be; and Cu-Al-Fe.

(5) Ammonia in some form is the fifth (and also obvious) condition necessary to cause ammoniacal SCC. There are almost unbelievably diverse and obliging sources of ammonia, including the decay of all sorts of by-products of many living organisms and the decay of the organisms themselves, electrical storms, spark discharges, some soldering fluxes (NH_4Cl), and agricultural and industrial chemicals. Three examples which have caused SCC in phosphorized copper tubing used in heating systems will illustrate the diversity of ammonia sources: (a) amines used as foaming agents in foamed concrete used to insulate underground pipes (b) latex adhesives used to lay vinyl tile on floors pierced by copper tubing, and (c) ammonia-containing agents used to clean those floors. Not only can ammonia be produced by a wide variety of reactions,

TABLE III

Relative susceptibility of copper alloys to ammoniacal SCC*

Very low susceptibility:	Cupronickels,** tough pitch copper, silicon bronze***
Low susceptibility:	Phosphorized copper
Intermediate susceptibility;	Brasses containing less than 20% Zn, such as red brass. commercial bronze, aluminum bronze, nickel silver, phosphor bronze, and gilding metal.
High susceptibility:	Brass containing over 20% Zn, with or without small amounts of Pb, Sn, Mn, or Al (such as leaded brass, Naval brass, Admiralty brass, manganese bronze, or aluminum brass). The higher the Zn, the higher the susceptibility.

*After Thompson (3).

**For lowest susceptibility, the iron in 90-10 cupronickel should be solutionized

***But note that this alloy is highly susceptible to SCC in high temperature steam.

but additionally there is some evidence that the ammonia so produced in dilute solution can be concentrated in corrosion pits by an unexplained process. It is not uncommon for evidence of ammonia <u>surmised</u> to have caused SCC to be missing at the time for analyzing a failure which may be done long after the cracked item has been removed from the environment causing cracking and has been dried. More on this below.

Organic amines and hydrazine cause copper alloys to crack (if oxygen is present), and it is sometimes implied that they do so by first decomposing to ammonia. As an alternative possibility, perhaps they simply perform a complexing role directly with the intermediate decomposition (4). In any event the presence around copper alloys of any nitrogenous compound which has the capability of forming complexes even resembling the cupric-ammonium complex should be considered as potentially causative of SCC as ammonia unless proven otherwise.

The effect of ammonia concentrations on cracking kinetics in various alloys is not known quantitatively. There is a recently adopted ASTM Standard Recommended Practice for ammoniacal SCC tests at one constant ammonia concentration, designated ASTM G 37-73, but this test is valid for binary Cu-Zn alloys only. It is being modified to include Cu-Ni-Zn alloys (nickel silvers).

* * * * *

Even if all five of the above conditions are met, and if among these stress, susceptibility, and ammonia concentration are at near maximum hazardous levels, ammoniacal SCC doesn't necessarily occur immediately. There is a finite period available to take preventive measures, although there are no quantitative rules available to fix the length of the grace period. An example will be cited, however, which will permit deducing something about the length of this period for one set of conditions.

The presence of CO_2 is not a necessary condition for cracking, but it is observed to speed up the process markedly. Corrosion pits or other stress intensifiers also do not seem to be necessary conditions for initiating ammoniacal SCC, but some service experience suggests that plug type dezincification may speed up the initiation. Corrosion pits may also act as ammonia concentrators and/or concentrators of other chemical species.

Cases illustrating principles

(1) A case of liquid attributed to deliquescence. Springs used in central office telephone equipment were made of highly cold worked nickel silver (nickel brass) (C 757 00) and installed in a nominally dry space with provision for air cooling from the outside atmosphere. (Ref. 5) Some of the springs ultimately failed by SCC. Let us check out our five necessary conditions: Water was not expected to be present, at least in the condensed phase, but atmospheric oxygen, high stress, and at least intermediate susceptibility were present, and one might assume the possibility of ammonia unless conditions were such as to afford confidence of its exclusion. The problem was to explain how, in air of low humidity, the moisture requirement was met. Careful examination revealed the presence of particles of airborne solids, including

nitrates, which could deliquesce in air having a relative humidity as low as 55%. As a result of laboratory tests with these solids, the condensate so produced on the brass surface from air of low humidity was concluded to account for the cracking observed in service. Incidentally the airborne nitrate turned out to be ammonium nitrate which is used as a fertilizer.

The tactic chosen to control the problem was to switch to a less susceptible alloy, cupronickel. High stress and the same environment including presumably the same ammonia source were still present, but substituting an alloy two categories lower in susceptibility was found to afford the necessary security. One might postulate alternative measures such as filtering out the airborne particles, or zinc coating, about which more below.

This case illustrates an important concept that with water and oxygen requirements met, the probability of cracking is a function of the joint action of the stress, susceptibility, and ammonia concentration. This extremely important practical relationship is not quantifiable by existing data, and one is reduced to using qualitative terms. In the nickel silver instance the stress was certainly high, the susceptibility intermediate, and the ammonia concentration perhaps low (but not necessarily so locally due to possible decomposition of nitrate).

Lowering the susceptibility factor rather drastically by the substitution of cupronickel sufficed to avoid SCC even though the other factors remained unchanged.

(2) Annealing usually avoids the problem but in one case was not done soon enough. High-zinc brass is rolled to form the screw shells used as bases for incandescent light bulbs and plug fuses. The stresses after forming are high, the susceptibility of the material is in the highest category, and one could confidently predict that in service or in storage many of the shells would eventually encounter enough water, ammonia and oxygen to satisfy all remaining conditions for cracking. But ammoniacal SCC does not occur instantaneously, and there is usually ample time to get the cold-formed shells into an annealing furnace to remove the forming stresses. After proper annealing the stress is sufficiently low to avoid trouble.

But there was trouble in one case described by Thompson (Ref. 3): During a cold New England winter one lot of shells cold-formed in one building of a plant was trucked to another building to be annealed. If the shells had gone into the annealing furnace at once all would have been well, but this particular lot arrived in the annealing building too late on a Friday afternoon to be annealed that week, and on the following Monday morning the shells were found to be cracked by the thousands. Let us analyze this case by inventorying the necessary conditions for cracking. The stress and susceptibility were high, there was presumably at least a trace of ammonia present in the annealing building perhaps from chemical processes, and of course, atmospheric oxygen was present. But what about the requirement for moisture? The annealing building was warm, with air particularly humid from nearby pickling and cleaning operations. The cold shells at lower than room temperature undoubtedly picked up a thin film of moisture which along with even a trace of ammonia would be sufficient to complete the necessary conditions for cracking. If the lot had been warmed and dried with hot air, or even more simply if it had been left outside in the cold, dry air, the cracking would probably have been avoided. Of course, the safer procedure would have been to modify the schedule to ensure annealing immediately after forming. The incident shows us that for these conditions the time allowed to get the annealing started before cracking starts was something less than about 2 1/2 days.

(3) Sometimes materials of "low susceptibility" crack. Phosphorized copper (C 122 00) is used for water pipe in great quantities. The allow has a low susceptibility to ammoniacal SCC, and in straight lengths it is commonly supplied in the fully hard condition. But the stresses from cold forming might be expected to relax at least partially because of room temperature creep, and in any event the experience is that ammoniacal SCC of this

material is extremely rare. The susceptibility is low, but the stresses as formed are high. There is usually adequate oxygen and moisture, and enough ammonia is produced somewhere to cause the rare failures. In one instance the cracking initiated from the outside and was attributed to ammonia produced by the decomposition of damp animal hair in felt insulation surrounding the pipe. In two other cases the ammonia was concluded to have been formed by microbial decomposition in cooling water. In another pair of cases involving residential piping, the stresses were atrributed to straightening of coiled pipe, and the ammonia was surmised to have come from lawn fertilizer. To emphasize the rarity of the occurrence of SCC in this material, it is instructive to note that the two cases cited last were the only two failures reported out of 50,000 installations in the same area. Annealing is an obvious way to reduce the hazard if in a critical component which would justify the special treatment.

(4) Many highly susceptible alloys are used successfully. Many tube-and-shell heat exchangers are used both for main condensers and for auxiliaries in various kinds of steam power plants. These may be tubed with cupronickel, particularly in naval power plants, but for economy reasons central station power plants are largely tubed with aluminum brass or with Admiralty brass,

both highly susceptible to ammoniacal SCC. Although the brass tubing is customarily supplied in the fully annealed condition and the cupronickel tubing (less susceptible) in the stress-relieved condition, when it is expanded to form the seal at the tube sheet dangerous stresses may be introduced in the tube if the rolling tool is allowed to extend beyond the inner edge of the tube sheet. In such circumstances the tube is expanded, and stresses are produced in the outer surface of the tube. As if this were not enough of a hazard, on the steam (shell) side ammonia may be present due to decomposition of amines sometimes used to control corrosion, or perhaps the amines may play the essential complexing role directly without need to be converted to ammonia, as indicated above. Additionally, on the water side (tube interior) there is always the possibility of ammonia being produced from decaying organic matter in the riverine, estuarine, or sea water widely used to cool the condensers. Let us see how, with stressed susceptible alloys very probably in the presence of ammonia (or adequate substitute), it is possible to control the cracking problem well enough for these alloys to be viable candidates as materials of construction.

In a well designed and well operated plant, the oxygen level on the steam side outside the air-removal section is low, low enough to effectively remove that one necessary condition for cracking in all but exceptional cases. (In the air-removal section where oxygen can be high and ammoniacal compounds are likely, alloys susceptible to SCC are avoided). On the tube side the sluicing through of the cooling water is almost always adequate to prevent the build-up of dangerous levels of ammonia, and failures originating on the water side are very rare.

Note that the practical solution is to use two partial measures, (1) the tubing is stress relieved if cupronickel or fully annealed if brass, and care is taken not to introduce too much assembly stress (difficult to avoid), and (2) the oxygen is kept low on the steam side, and the ammonia is kept low on the water side.

When the system is shut down, new hazards must be considered. On the shell side oxygen can leak in and, if added to amines or residual ammonia and water, can fulfill the conditions for cracking. On the tube side any ammonia produced by the decomposition of organic matter is no longer being diluted by incoming water, and dangerous levels of ammonia may build up. If either side is drained, there is a hazard that water and ammonia sources may remain in pocketed zones and in sagging tubes. Two strategies are available to avoid the cracking problem on each side of the condenser. If design permits, the shell side can be filled with clean deaerated water, which should minimize in-leakage of oxygen and also minimize the concentration of residual ammonia; or it can be drained, thoroughly dried, and blanketed with nitrogen for extra insurance. The tube side can likewise be filled with water and left so; or it can be drained, dried, and possibly additionally filled with nitrogen. The most hazardous lay-up situation is to allow either side to remain partially covered with water. Thorough drying is the preferred stabilizing procedure during a long lay-up.

It is a common occurrence for a completely fabricated condenser or other heat exchanger tubed with aluminum brass or Admiralty brass to be delivered to the site where a large fossil-fuel or nuclear power plant is scheduled to be built three years or even more before the plant is finally completed. The condenser already has the highly susceptible alloy condition met, frequently with stresses from tube straightening and rolling. If on the construction site rain or condensate furnishes water and the atmosphere provides the oxygen, only ammonia remains to be supplied to complete the conditions for cracking. The addition of this last remaining condition has obviously happened in a number of recent plants, for units intact at the time of shipment have been found cracked at installation a few years later. Proper packaging to exclude water and also ammonia is an obvious step to avoid this problem.

Incredible as it may seem there have been a few cases in which completed condensers were leak-tested on the plant site using ammonia as the pressurizing fluid! The other four conditions were already met for cracking, and the ammonia factor was now high. Needless to say the condensers were ruined. One tube sheet was cracked completely through its 2-inch thickness. (Ref. 6)

(5) Household articles such as coffee urns and metal goblets sometimes illustrate the SCC phenomenon. Cold-formed articles in this category are often made of brass, plated (often one side only) with chromium or silver. They may serve intact for a long time and then exhibit rapid cracking. In some instances the onset of cracking has been definitely associated with exposures to enhanced levels of ammonia, such as the unfortunate use of a cleaning compound high in ammonia, formulated for use on copper but not suited for brass. Since there is no nondestructive way to ascertain the degree of stress relief (if any) in these low-technology items, the only prudent policy is to minimize access of ammonia.

SCC IN OTHER ENVIRONMENTS

Industrial and marine environments. Moist air containing as little as 5 ppm of sulfur dioxide can cause SCC (Ref. 7). It is thus not surprising that a recent extended systematic test program (Ref. 8) showed that an industrial atmosphere (New Haven, Connecticut), badly contaminated with sulfur dioxide but essentially free from ammonia, caused cracking of many alloys. By contrast only a few alloys cracked in the marine atmosphere. The findings of the program, greatly condensed, are shown in Table IV. It is typical of the complexities of SCC that at high concentrations of sulfur dioxide (>0.1% by volume in air) copper alloys do not crack, but they corrode (Ref. 9). Ammoniacal stress corrosion cracks are tarnished, whereas sulfur dioxide cracks are bright.

TABLE IV*

SCC BEHAVIOR OF WROUGHT ALLOYS IN
INDUSTRIAL AND MARINE ATMOSPHERES

INDUSTRIAL	Alloys which cracked: C 260 00**, 353, 443, 672, 687, 688, 762, 766, 770, 782
	Alloys did not crack, 2.2 years or longer: 110, 194, 195, 230, 405, 411, 422, 425, 510, 521, 619, 638, 706, 725, 752
MARINE	Alloys which cracked: 672, 766, 770, 782
	Alloys which did not crack, 2.2 years or longer: All the alloys shown under INDUSTRIAL except these four above.

*After Ref. 8.

**Omitting thenceforward the prefix "C" and the suffix "00".

High tensile alpha-beta brass has been used for fasteners in sea water, but because of cracking it is being replaced by either aluminum bronze or silicon bronze

(Ref. 9). Maganese propeller bronze (C 861 00) has been observed to undergo SCC in sea water, attributed by some to biologically produced ammonia, but by some simply to water; this bronze contains both alpha and beta phases, and heat treatment plus care to keep the composition within specified limits to reduce the amount of beta has been reported effective in lowering the incidence of SCC. Cracking of bronze propellers has also been reported in some cases where cathodic protection has been applied to the hull and therefore probably to the propellers; perhaps this is a form of hydrogen embrittlement.

Miscellaneous environments. SCC has been observed in the field (and confirmed in the laboratory) when nitric acid fumes react with stressed brass; whether or not the ammonium ion, as a decomposition product of nitric acid, is involved does not seem to have been established. SCC has been observed in the laboratory when brasses are stressed in the presence of aqueous solutions of sulfate, nitrate, acetate, tartrate, or citrate which also contain copper ions. There is some evidence that oxides of nitrogen (generating ammoniacal species?), carbonates, and phosphates can cause SCC of some copper alloys.

Common aluminum bronze D (C 614 00) is susceptible to SCC in plain live steam. Minor additions of alloying elements, (especially about 0.2% Sn) as in a proprietary grade of the same basic bronze has been reported helpful in avoiding the problem (Ref. 10). Silicon bronze is also susceptible to cracking in steam to the extent that one authority arbitrarily places a temperature limit of 120°C (230°F) on the steam if silicon bronze is to be used with it (Ref. 9).

None of these miscellaneous corrodents has received anything approaching the amount of systematic study that ammonia has received. The lesson here is that if one is concerned about a fundamentally new combination of copper alloy and chemical environment compared with any studied in the laboratory or experienced in service, there is no adequate substitute for conducting a realistic test of compatibility.

Liquid metal cracking. Certain liquid metals cause stressed copper alloys to crack. Mechanistically this process is certainly different from SCC in aqueous solutions in at least some aspects and it is usually called liquid metal embrittlement, not SCC. But from a practical standpoint it will be treated here together with the other forms of sustained load cracking which the design and maintenance engineer must control.

Mercury (Hg) is particularly troublesome to copper alloys, and neither metallic Hg nor its compounds should be permitted to contact copper alloys. Thompson illustrates the seriousness of the trouble that can be caused when this stricture is violated:

> "A small brass heat exchanger had been manufactured. It was vacuum tested using a Hg manometer to check the vacuum. A slug of Hg was accidentally allowed to enter the heat exchanger. This was known and the heat exchanger was opened and the Hg was cleaned out, presumably perfectly. The heat exchanger was one of four that were used as chillers in the air conditioning of a submarine. It was installed outboard of the keel on the lowest deck. After the vessel was completed and launched, the system was pressure tested and it was found that the chiller leaked. The only way to remove the chiller was to cut holes through every deck from the top of the submarine to the bottom, remove and replace the chiller, and repair weld all the decks. The chiller was, of course, the victim of liquid metal embrittlement from Hg. The dire warning is never trust Hg in contact with any copper metal." (Ref. 4)

Figure 1 shows a brass heat exchanger tube cracked by Hg.

The difference between Hg cracking and ammoniacal SCC is emphasized by the experience that cupronickel, highly resistant to ammoniacal SCC, is highly susceptible to cracking by Hg.

Molten solder, molten tin, and molten sodium have also been observed to cause cracking of stressed copper alloys.

MISCELLANEOUS MEASURES

Coatings of course are not an attractive way to control the SCC problem on heat exchanger surfaces, but organic coatings have been reported useful in preventing or delaying SCC in other situations, such as phenolformaldehyde films on cartridge brass. Systematic data in the open literature are lacking. Chromium plates and nickel plates have not been found effective in the situations in which it is practical.

Metallic zinc coating has been reported to be highly effective, on the other hand. The zinc may act partly as a barrier, but there is evidence that additionally cathodic protection from the zinc can prevent cracking at openings in the coating. If zinc coating and cathodic protection can be proven dependable control measures, they may be found useful in many more situations than now employ them.

Benzotriazole either as a surface treatment or as an inhibitor in the environment may be useful in preventing SCC in marginal situations.

DIAGNOSING SCC

Even in alloys highly ductile in a tensile fracture, all stress corrosion fractures (and those produced by liquid metal cracking) are macroscopically brittle. Particularly when they are caused by complex residual stress fields from forming operations the cracks may be branched, but not necessarily so. Multiplicity of cracks, whether more or less parallel to each other or diverging, is highly indicative of SCC, but absence of multiplicity or of branching is by no means a basis for excluding SCC.

If a crack path is examined by standard optical methods and found to be intergranular (Figure 2), either SCC (including ammoniacal SCC) or liquid metal cracking can be assigned as the cause. If the cracking is caused by Hg, it is inevitably intergranular, and there may be enough Hg amalgamated with the metal of the crack walls to be readily detected by standard chemical analysis. Cracking by Hg in metals at high temperatures, however, may leave so little Hg that special spectrographic trace analysis methods may be required to detect it.

If the crack path is found to be transgranular, SCC can still be the cause (Figure 3). Whether the crack path is intergranular or transgranular is a complex function of alloy composition and electrochemical factors, and few reliable simple rules are available to specify crack path choice. One such rule, however, is that in alpha-beta alloys the SCC path is intergranular between alpha grains and transgranular across beta grains; in all-beta alloys SCC is predominantly transgranular.

Fatigue cracks are also transgranular, whether across alpha or beta grains. Transgranular SCC usually is branched; except for aluminum brass it is usually associated with some intergranular cracking and with some change in direction as a transgranular crack crosses a grain boundary. One practical rule for commencing the distinction between fatigue and SCC from optical microscopy on a polished section is as follows: If the crack is transgranular and blunt ended, it is probably not SCC but fatigue. If it is transgranular but sharp ended, look further into the failure conditions, such as the possibility of vibrations or other cause of reciprocating stress, before ruling out fatigue. Although most transgranular SCC is associated with some intergranular cracking (except for aluminum brass), fatigue cracks almost never propagate even partially along a grain boundary, and they tend not to deviate when passing from one grain to another. A definitive distinction of fatigue from SCC is available with electron fractography by which fatigue can be positively identified by its characteristic striations. Striations from plastic cross slip are sometimes seen on SCC fracture surfaces, but they lack the special features which are conclusively diagnostic of fatigue striations. In summary, in a normally ductile copper alloy a brittle crack lacking genuine fatigue striations may be diagnosed as SCC unless Hg (or other metal liquid at some point in the history of the part) is present indicating liquid metal cracking.

THEORY

As in all other systems, SCC in copper alloys is caused by the strain induced activation of the metal in the vicinity of the crack tip and the consequent reaction of the active metal locally with the corrodent within the crack. There is considerable (though not universal) agreement about how the strain activates the corrosion process and how the consequent reaction occurs for the case of alpha brasses in the ammoniacal environments which tarnish them. The model is basically as follows: Copper in the alloy reacts first to produce with ammonia a complex ion, then the copper in the complex ion reacts with hydroxyl ions to produce cuprous oxide. The cuprous oxide grows into the metal from which the copper is derived and would stifle further reaction unless a separate process occurred. At this stage two views have been advanced to account for crack growth. One view is that the cuprous oxide film, which tends to intrude along grain boundaries, is brittle and eventually cracks to expose bare (reactive) metal at the end of the crack. A new layer of oxide forms at this point and eventually cracks also. This sequence is shown in Figure 4. Another view is that the dislocation arrays in the stressed metal are blocked at barriers and that the growth of the cuprous oxide at the expense of underlying metal destroys some of the blocking action, permitting highly localized plastic flow of the metal to rupture the oxide layer and expose bare metal for the beginning of another cycle. Thus the one view is that the metal is exposed by the cracking of a brittle oxide, the other is that dislocation unlocking by corrosion permits plastic flow of the metal to punch through a (ductile) oxide film.

The chemical reactions may be written as follows (Ref. 11):

Dissolution reaction: $Cu + nNH_3 + \frac{1}{2} O_2 + H_2O \rightarrow Cu(NH_3)_n^{2+} + 2OH^-$

Cathodic reaction: $Cu(NH_3)_5^{2+} + e \rightarrow Cu(NH_3)_2^+ + 3NH_3$

Precipitation reaction: $2Cu(NH_3)_2^+ + 2OH^- \rightarrow Cu_2O + 2NH_3 + H_2O$

We can now account for the four factors (other than inherent susceptibility) which combine to cause ammoniacal SCC: The ammonia is required to take up the copper as a solution complex; the oxygen generates the hydroxyl ions which precipitate the cuprous oxide, and additionally oxygen is observed to be required to dissolve copper initially; the water serves both as a solvent for the copper ammonium complex and is recycled between the dissolution reaction and the precipitation reaction; and the stress serves to bare metal by either cracking the oxide film or by causing the metal to flow through the film plastically, reinitiating the cycle of film growth and rupture. Recent observations have suggested that this theory may require modification.

The theory of SCC by other mechanisms has not been worked out to the point of general acceptance and will not be included here. Readers interested in this aspect will find Ref. 11 a useful starting point.

SUMMARY

Most service failures by SCC in copper alloys are caused by the conjoint action of five factors, (1) water, (2) oxygen, (3) tensile stress, (4) alloy composition and structure, and (5) ammonia or perhaps alternatively ammonia-like complexing agents. Sulfur dioxide can also be responsible for SCC in industrial atmospheres.

Alloys have been classified in four categories of susceptibility. Examples have been given illustrating the roles of each of the five factors.

Although in principle one might think to avoid SCC in a given case by decisively controlling one of these five factors, uncertainties about the precise nature of the environment and about the stresses in assembled and functioning components in real life situations often lead to a strategy of a multiplicity of control measures any one of which may not be amenable to exact control.

There are believed to be several mechanisms of SCC depending upon environment and alloy, but the model widely believed responsible for most service failures involves the periodic formation and rupture of a film of Cu_2O.

Mercury and its compounds must be kept away from copper alloys at all costs.

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Figure 1

Admiralty brass condenser tube failure induced by accidental exposure to mercury in a marine condenser. Courtesy of S. D. Reynolds, Jr., and F. W. Pement, Westinghouse.

Figure 2

Intergranular stress corrosion cracking of Admiralty brass condenser tubing (500x). Courtesy of S. D. Reynolds, Jr., and F. W. Pement, Westinghouse.

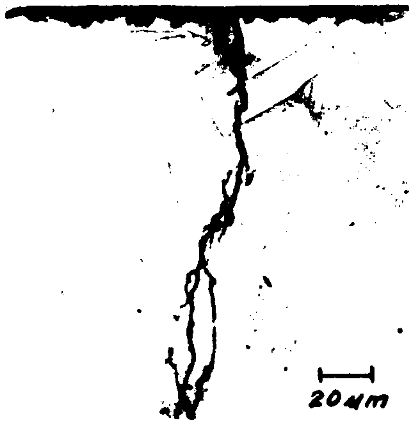

Figure 3

Transgranular stress corrosion cracking of Admiralty brass condenser tubing. Courtesy of S. D. Reynolds, Jr., and F. W. Pement, Westinghouse.

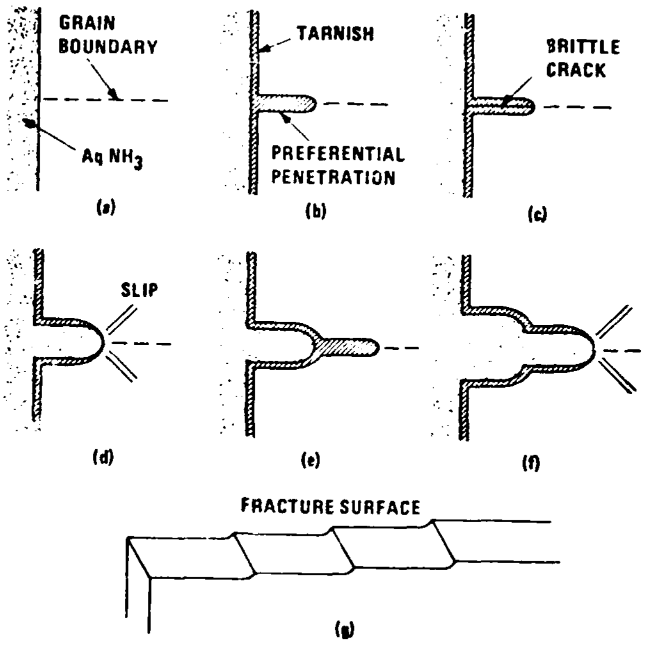

Figure 4

Schematic illustration of the tarnish-rupture mechanism for SCC of alpha-brass in tarnishing solutions. The tarnish is considered to grow preferentially along a grain boundary (b), until it undergoes brittle fracture (c). The crack is arrested by slip in the substrate, exposing the metal to the environment (d). Further intergranular penetration then occurs (e), leading to further limited fracture (f). Crack propagation thus proceeds by repeated cycles, the resulting fracture surface showing evidence of discontinuous fracture (g). (Pugh, Ref. 11)