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# EROSION CORROSION RESISTANCE OF CHROMIUM AND NIOBIUM MODIFIED 70/30 COPPER NICKEL ALLOYS FOR SEAWATER PIPING SYSTEMS

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# ABSTRACT

The firemain system on Canadian warships was designed to be fabricated by silver brazing. Over the past number of years, some difficulties have been encountered when employing the brazing technique. To overcome these difficulties it is being proposed that the firemains on the new ships be of an all welded construction. An additional benefit will be a reduction in the overall weight of the firemain system. The erosion corrosion resistances of two potential replacement weldable alloys with sufficient strength were evaluated: cast chromium modified 70/30 copper nickel and cast niobium modified 70/30 copper nickel. For comparison purposes the present firemain materials, wrought 90/10 copper nickel and cast leaded tin bronze (ASTM B61), were also tested. The weight loss of each alloy was measured after exposure to impingement attack by a seawater jet mixed with air bubbles. Cast chromium modified 70/30 copper nickel in both the welded and parent metal conditions had greater resistance to erosion corrosion under the severe conditions to which the alloys were exposed than the niobium modified alloy. The parent metal of the chromium modified alloy exhibited erosion corrosion resistance that was as good as or better than that of the presently employed materials, but the weld metal of the chromium modified alloy was generally not as resistant.

## SOMMAIRE

Le collecteur d'incendie équipant les navires de guerre Canadiens est conçu pour être brasé à l'argent. Au cours des dernières années cependant, le brasage a causé certaines difficultés que l'utilisation de collecteurs d'incendie entièrement soudés sur les nouveaux navires a permis d'éliminer. Le poids total moindre de ce genre de collecteur constitue un avantage s'ajoutant à ceux qu'offre déjà la construction soudée. Deux alliages soudables, résistants à la corrosion par érosion et susceptibles de remplacer l'alliage actuel, ont été évalués: le cupronickel coulé 70/30 modifié au chrome et le cupronickel coulé 70/30 modifié au niobium. Pour fins de comparaison, il est intéressant de noter que les collecteurs d'incendie actuels sont composés de cupronickel battu 90/10 et de bronze coulé à l'étain (ASTM B61). Ces alliages ont également été mis à l'essai. Les pertes de poids subies par chaque alliage ont été mesurées après exposition à un jet d'eau de mer mélangé à des bulles d'air. La résistance à la corrosion par érosion dans des conditions extrêmes du cupronickel coulé 70/30 modifié au chrome composant à la fois le métal de base et le métal de soudage a été supérieure à celle de l'alliage modifié au niobium. L'alliage modifié au chrome du métal de base a démontré une résistance à la corrosion par érosion aussi bonne que celle des alliages utilisés actuellement, et même meilleure. Tel n'a pas été le cas de l'alliage modifié au chrome du métal de soudure qui, en général, n'a pas donné des résultats aussi satisfaisants.

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# INTRODUCTION

The firemain system on a warship provides large volumes of seawater for a number of different applications. It supplies large amounts of water for fire fighting, and from smaller branch lines, water for such systems as condensers and heat exchangers. The firemain systems on existing Canadian Forces ships were designed so that they could be fabricated by silver brazing. This fabrication technique has resulted in a number of brazing problems at the fittings.

The method used to draw seawater from a pipe at 90° into a smaller diameter pipe involves the use of a brazolet (Figure 1) rather than the traditional but heavier cast tee. Obtaining the correct fit-up clearances for capillary action between the brazolets and larger diameter pipes is very difficult, particularly in situ. Consequently, the majority of the joints end up with a fillet braze without face to face bonding and a resultant propensity for leaking.

An additional brazing problem that has been experienced occasionally is that of liquid metal embrittlement of the copper nickel pipe. This type of problem normally occurs when brazing larger diameter pipe. In an attempt to ensure that there is enough capillary action of the silver braze, the pipe may be overheated. As a result, silver may penetrate the grain boundaries of the pipe, thereby reducing the strength of the alloy and resulting in cracking (Figure 2). One other consequence of overheating is a reduction in the erosion corrosion resistance of the alloy as a result of grain boundary melting[1].

Leaks at brazed flange/pipe joints (Figure 3) have occurred at specific locations in the firemain systems. The cause is attributed to design problems, whereby these locations experience periodic loadings which are too high for even a correctly brazed joint.

In order to eliminate these brazing problems, it has been proposed by the Director, Maritime Engineering Support (DMES) that future firemain systems be of all welded construction. The systems could be fabricated and repaired with greater ease and would be capable of handling higher loads. In addition, the weight of the firemain systems would be reduced because fewer and smaller flanges would be required.

There would still be a requirement for valves and elbows as well as some tees and flanges. Unfortunately, the present material used for these fittings, cast ASTM B61 leaded tin bronze, cannot be used as it is not weldable. Consequently, it is necessary to find a suitable replacement alloy. Two cast alloys were chosen for intensive evaluation: a standard cast 70/30 copper nickel alloy modified with niobium and a non-standard chromium modified cast 70/30 copper nickel alloy (IN 768).

A study of the foundry characteristics, weldability and mechanical properties of these alloys was carried out at Energy, Mines and Resources Canada[2-5]. Briefly, it was found that both alloys could be cast satisfactorily to specifications (ASTM B369). Production type castings could be readily made. In fact, a six valve chest for an Oberon class submarine has been cast using niobium modified 70/30 copper nickel. Similarly, an impeller for a hull and fire pump on a DDH 280 class destroyer has been cast using chromium modified 70/30 copper nickel. The weldability of both alloys was assessed using gas metal arc (GMA) welding. Two different electrodes were evaluated for the niobium modified alloy, Monel 67 and Cuprotode 521, with the Cuprotrode 521 being eventually chosen as the most suitable, as satisfactory mechanical properties could not be obtained using the Monel 67. A Monel 451 electrode was used to weld the chromium modified alloy. Although there appeared to be more defects associated with welding the chromium modified alloy, the weldability was considered to be satisfactory.

This study was initiated to evaluate the erosion corrosion resistances of cast niobium and chromium modified 70/30 copper nickel alloys. For comparison purposes, wrought 90/10 copper nickel and cast leaded tin bronze (ASTM B61), both presently used in the firemain system, were also included in the study.

## EROSION CORROSION OF COPPER NICKEL ALLOYS

Erosion corrosion is said to be occurring when a metal suffers accelerated attack while exposed to a flowing corrodent. Copper nickel alloys, chosen for marine systems because of their useful antifouling properties, good corrosion resistance and general immunity to stress corrosion cracking, are susceptible, under some conditions, to erosion corrosion damage.

The variables which determine the extent of erosion corrosion of copper nickel alloys in seawater have been studied extensively[7]. The environmental variables which affect the erosion corrosion of a seawater system are velocity, oxygen content, temperature, pH and entrained gases or solids. Some system variables such as pipe diameter and surface roughness determine the seawater flow pattern and its continuity, while metallurgical variables and alloy composition determine an alloy's ability to form a protective surface film. All three sets of variables affect erosion corrosion.

Many studies have been conducted on the relationship between alloying element additions and their effects on the protective film formation characteristics of copper nickel alloys. It has been established that small additions of iron are necessary in copper nickel alloys for good corrosion resistance in seawater environments[8]. It has also been reported that the effect of chromium additions on erosion corrosion resistance is especially dramatic[9].

The beneficial effects of alloying additions can probably be explained in terms of one or more mechanisms, as follows[7].

1. A superior physical barrier is created between the metal and the corrodent as a result of the formation of a protective surface film with improved strength, tenacity and flawlessness.
2. The ionic or electronic transport through the corrosion product is reduced.
3. The cathodic reaction (oxygen reduction) is polarized.
4. The rate at which the protective film is restored after deterioration is increased.
5. The hardness, strength and metallurgical structure of the metal is changed.

Chromium is well known for the protective surface oxide films it forms on stainless steels and, therefore, gives support to the first mechanism. The work of Popplewell, et al[10] supports the second. They found that when 90/10 copper nickel was modified with iron, doping of the $Cu_2O$ corrosion product by iron ions significantly increased the electronic resistance of the film and also decreased its corrosion rate. The third mechanism is supported by work on copper iron alloys conducted by North and Pryor[11]. They found that iron incorporated into the corrosion product as $\gamma$-FeO·OH acted as a cathodic inhibitor, increasing the cathodic polarization.

It has also been suggested that the onset of accelerated erosion attack is due to something other than strict electrochemical corrosion phenomena[12]. Copper base alloys have been shown to be susceptible to a critical surface shear stress in flowing seawater. This value is a measure of the force applied by moving seawater to the corrosion product film at the sample surface and is a function of seawater temperature, density, viscosity, salinity and flow pattern. The film degrades and is physically removed when the surface shear stress in the fluid exceeds the binding force of the adherent corrosion product film. Alloying element additions are believed to contribute to the adherence qualities of a corrosion product in addition to its electrochemical nature.

In any piping system, no matter how turbulent, there will always be a laminar layer adjacent to all surfaces. It has been suggested that the thickness of this boundary layer which determines the rate of mass transfer (diffusion of $O_2$ and $CO_2$ toward the metal and $Cu^{2+}$ and $Cu^{+}$ away from the metal) is the most critical flow dependent variable. The magnitude of the surface shear stress in a fluid is a direct measure of the boundary layer thickness.

It is seen, then, that the removal rate of metal as a result of erosion corrosion is a complex function of both fluid dynamic and environmental variables as well as metallurgical variables which determine the physical and electrochemical nature of corrosion products.

## EXPERIMENTAL PROCEDURE

The resistance of the copper nickel alloys to erosion corrosion was evaluated at DREA using a device patterned after the work of Bengough and May[13]. They found that erosion corrosion or "impingement" attack on condenser tubes could be reproduced and studied satisfactorily in the laboratory by subjecting suitable test pieces to the action of a submerged jet of salt water mixed with air bubbles. DREA's jet impingement apparatus is shown in Figure 4.

Because it has been previously established[14] that copper base alloys exhibit excellent corrosion resistance at low velocities, but are subject to degradation by erosion corrosion at high and intermediate velocities, it was the intent of this investigation to determine which of the alloys of interest suffered the least degradation under a relatively high velocity. In particular, a jet of seawater was impinged on each sample at 12.2 m/sec. Turbulence was promoted in the seawater jet by entraining it with 3.4% air. The severe turbulence and velocity of the jet served to increase the erosion corrosion rate to a value measurable within a shorter period of time.

Behrens et al[15] determined that variations in the dissolved oxygen content of seawater at low concentrations can have a significant effect on the erosion corrosion resistance of copper nickel alloys, while the effect of variations at higher dissolved oxygen concentrations are not significant. Accordingly, the effects of any variations in the high dissolved oxygen content of the jets entrained with 3.4% air would be insignificant.

The temperature of the seawater jets ranged seasonally between 2 and 16°C. Previous investigations have shown that the corrosion rate of copper based alloys in flowing aerated seawater may increase[15], decrease[16,17], or may only change slightly[8,18], when the temperature of the water is increased. The disagreement in the reported effects of temperature is undoubtedly due in part to the variations in the oxygen content of the waters tested.

In this investigation, samples with dimensions of 38 x 76 x 6 mm were machined from the alloys and finished to 320 grit. Each sample was weighed prior to a test and then attached to a specimen holder as shown in Figure 5. After preselected exposure times, the samples were removed from the apparatus, cleaned according to ASTM G1-72 (Standard Recommended Practice for Preparing, Cleaning, and Evaluating Corrosion Test Specimens), and weighed. The weight loss per unit area of exposed metal was then calculated for each sample. The samples were refinished to 320 grit before subsequent exposures.

The eroded surfaces were examined by scanning electron microscopy (SEM) and were chemically microanalyzed by x-ray energy spectroscopy (XES). Metallographic examinations were also made of sectioned specimens.

The tests were carried out on both as-cast and welded samples obtained from PMRL, on a wrought 90/10 copper nickel alloy (UNS C70600) and on a cast ASTM B61 leaded tin bronze (UNS C92299). The latter two alloys are presently used in the firemain system. A minimum of fourteen data points was obtained for each alloy. The chemical compositions of these alloys are shown in Table I, along with those of a standard wrought 70/30 copper nickel alloy (UNS C71500) and a nonstandard chromium modified wrought 70/30 copper nickel alloy (IN 732). Table II shows their mechanical properties. The chemical compositions of the GMAW electrodes used to fabricate the welded samples are shown in Table III. The conditions under which the niobium modified 70/30 copper nickel alloy samples were fabricated are outlined in Table IV.

It was initially intended to compare the erosion corrosion rates of welds with those of heat affected zones (HAZ). Two separate groups of samples were made: one with weld material at the centre of samples, and the other with HAZ material at the centre of samples (Figure 6). Because of the narrowness of the HAZ within the exposed samples, it was later realized that it was incorrect to associate the weight loss entirely with the HAZ. The erosion extended into both the parent metal and weld metal regions of the samples. The results from these two groups of samples were therefore combined into one group for each alloy. Approximately eighty percent of the surface area of the samples with weld material at their centres was either weld or HAZ material, while only fifty percent of the surface of the samples with HAZ material at their centres was either weld or HAZ material.

## RESULTS

The erosion corrosion weight loss per unit area versus exposure time data was plotted for each alloy as in Figure 7 in which all of the data obtained from the samples of as-cast niobium modified 70/30 copper nickel are shown. This data is scattered considerably (the most by any of the alloys) and accordingly, the data sets for each alloy were analyzed and compared statistically.

Each material's weight loss per unit area versus exposure time data set was fit to a functional relationship of the form:

$$y = mx$$

where y is weight loss per unit area, x is exposure time and m is the slope of the curve, using the method of linear least squares. In addition, the coefficient of determination for each data set, which is a measure of the goodness-of-fit of a set of points to a least squares straight line, was calculated as:

$$r^2 = \frac{(n\Sigma xy - \Sigma x \Sigma y)^2}{(n\Sigma x^2 - [\Sigma x]^2)(n\Sigma y^2 - [\Sigma y]^2)}$$

where n is the number of points in a set of data. When $r^2 = 1$, the correlation is said to be exact. When $r^2 = 0$, the data are said to be uncorrelated with a linear equation.

The sets of data were also systematically separated into subsets in different temperature ranges, according to the time of year at which each test was carried out, to test the suspected effect of temperature on the experimental results. A linear least squares analysis of each of these different temperature range data subsets showed that the goodness-of-fit increased 83% of the time by separating each material's data set into two subsets: samples exposed to water temperatures lower than 5°C and samples exposed to water temperatures higher than 5°C. The results of the analysis of each material's data set and two temperature range data subsets are shown in Table V.

The results of the erosion corrosion studies on the two as-cast 70/30 copper nickel alloys, on the wrought 90/10 copper nickel alloy and on the cast ASTM B61 leaded tin bronze are shown in Figures 8, 9 and 10. Figure 8 compares the results, using all of the data. Figure 9 compares the results, using the lower temperature range data subset. Figure 10 compares the results, using the higher temperature range data subset.

For the particular test conditions to which the samples were exposed, these Figures show that the chromium modified 70/30 copper nickel alloy has greater resistance to erosion corrosion than the niobium modified alloy whether all of the data is compared or the temperature range data subsets are compared. These Figures also show that the chromium modified alloy's erosion corrosion resistance is as good as or better than that of the present firemain materials: wrought 90/10 copper nickel and cast ASTM B61 leaded tin bronze.

The results on the welded chromium and niobium modified alloy samples are shown in Figures 11, 12 and 13. The chromium modified welds consistently have greater resistance to erosion corrosion than the niobium modified welds. It is also evident, when these Figures are compared with Figures 8 to 10, that the parent metals are relatively more resistant to erosion corrosion than the welds.

The results on the niobium modified alloy samples, welded under three different conditions, are shown in Figures 14, 15 and 16. The sample numbers in these Figures correspond to the numbers in Table IV. The 1800 samples, which were welded with Monel 67 electrodes, have a significantly greater resistance to erosion corrosion than the 1802 and 1788 samples, which were welded with Cuprotrode 521 electrodes, when all of the data are compared or when the higher temperature range data subsets are compared. There is little difference between the samples' resistance when the lower temperature range data subsets are compared.

Figures 17, 18 and 19 show that the erosion corrosion rates of all of the materials except one are higher when exposed to temperatures higher than 5°C than when exposed to temperatures lower than 5°C. The welded niobium modified 70/30 copper nickel 1800 samples are the only samples whose erosion corrosion rate is lower when exposed to the higher temperatures.

By comparing Figures 17 and 18 it can also be seen that the chromium modified alloy's weld metal is generally not as resistant to erosion corrosion as are the presently employed firemain materials. This comparison may not be fair, as weld metal performance is being compared with parent metal performance.

The maximum depth of attack for a set of welded samples exposed for an extended period of time (1644 hours) is shown in Table VI. The eroded surfaces of these samples are shown in Figures 20, 21 and 22. There was no indication of selective attack within either of the parent, weld or HAZ metal regions on any of the chromium modified samples as shown in Figure 20. The niobium modified samples, however, did show greater depths of attack within certain metal regions. Figures 21 and 22 show the unusually greater amounts of erosion attack that occurred along the interfaces of a weld pass within the centre of the weld and along the length of the HAZ, respectively.

The metallographic structures, as seen by optical microscope, of the 70/30 copper nickel alloys at their parent metal/fusion zone boundaries are shown in Figures 23 and 24. Their eroded surface topographies, after cleaning, as seen by SEM, are shown in Figures 25 through 32.

The results of the electron probe microanalysis carried out on the eroded surfaces of welded chromium and niobium modified 70/30 copper nickel samples are compared with the results of an analysis done on polished and etched samples of the same alloys at Energy, Mines and Resources Canada[3] in Table VII. These analyses confirm that the high peaks and ridges on the eroded surfaces, as seen in Figures 25 through 32, are indeed dendrites, while the low valleys are interdendritic regions.

The peak to peak distance on the eroded surface of the niobium modified 70/30 copper nickel alloy weld metal (Cuprotrode 521) was smaller (Figure 26) than the peak to peak distance on the eroded surface of the chromium modified alloy weld metal (Monel 451) (Figure 28). The surface of the niobium modified weld metal was also smoother than the chromium modified weld metal. The chromium modified alloy parent metal had greater surface relief (Figure 29), but had a smaller peak to peak distance than the niobium modified alloy parent metal (Figure 31).

## DISCUSSION

The extent of erosion corrosion damage of copper nickel alloys in seawater is determined by three variables: environmental, system and metallurgical.

This discussion will focus mainly on the effects of metallurgical variables. It is important to recall, however, that the data analysis indicates that temperature, an environmental variable, is a significant experimental parameter in erosion corrosion studies and suggests that temperature control would improve the technique of studying erosion corrosion. The significance of temperature has been found previously[8,15-18].

Briefly, the erosion corrosion studies show that as-cast and welded chromium modified 70/30 copper nickel is more resistant to erosion corrosion damage than as-cast and welded niobium modified 70/30, and that niobium free Monel 67 welding electrodes are more resistant than the higher strength Cuprotrode 521 welding electrodes which contain niobium.

The metallurgical characteristics of an alloy are determined by its alloying elements. Both chromium and niobium modified 70/30 copper nickel alloys exhibit coring, a cooling rate dependent characteristic of cast alloys, which results from the accumulation of rejected solutes between the growing dendrites. The compositional differences which exist between the dendrite and interdendritic centres have been identified[2,3]. The dendrite centres in the chromium modified alloy are enriched in nickel, iron, manganese, silicon and chromium, while the interdendritic regions are enriched in copper. The dendrite centres in the niobium modified alloy are enriched only in nickel, iron, silicon and niobium, while both copper and manganese are enriched in the interdendritic regions. Second phase nickel silicide precipitates are distributed in a vein-like structure in the interdendritic regions of both alloys. In addition, the chromium modified alloy has fine chromium silicide precipitates in its interdendritic region, while the niobium modified alloy has coarse niobium silicides.

The additional strength which the niobium modified copper nickel alloy has over the straight copper nickel alloy is derived from the precipitation of second phases. In addition to this mechanism, the strengthening of the chromium modified alloy also results from:

(i) spinodal hardening by chromium; plus

(ii) solid solution hardening by silicon.

When alloys containing 20 to 45% nickel with up to 4% chromium are cooled through the miscibility gap which exists in the copper-nickel-chromium system, the single face centered cubic (fcc) phase decomposes into two new fcc phases[19]. The coherency strains arising from this "spinodal decomposition" result in hardening[20]. Alloys containing up to 0.4% silicon derive considerable strengthening from solid solution hardening[21], while additional strengthening in the form of precipitation hardening exists for alloys with higher silicon contents.

The mechanisms by which each of the modified 70/30 copper nickel alloys is strengthened may determine the extent to which these alloys are protected from erosion corrosion. The mechanical nature of erosion corrosion attack supports the suggestion that the elemental contributions of chromium to the hardness, strength and metallurgical structure of 70/30 copper nickel are important in providing the alloy with its superior erosion corrosion resistance. Its enhanced resistance may also be attributed to the additional mechanism by which the chromium modified alloy derives its strength: solid solution hardening by silicon.

The strengthening mechanisms, however, do not explain the poor erosion corrosion resistance of the weldments with respect to their parent metals, and, in particular, the poor resistance of the higher strength Cuprotrode 521 electrode with respect to the Monel 67 electrode.

Previous investigations[4,22] have shown that hardness and strength decrease with increasing cooling rates of both chromium and niobium modified 70/30 copper nickel. The more rapid cooling rate of weldments, as compared to that of castings, suppresses the precipitation hardening process, which is one strengthening mechanism, thereby resulting in lower strength and lower erosion corrosion resistance. The more rapid cooling of chromium modified weldments would not affect the alloy's strength and erosion corrosion resistance to the same degree since the spinodal hardening process would not be suppressed.

A previous investigation[4] on the weldability of niobium modified 70/30 copper nickel found that tensile specimens from 1800 samples welded with Monel 67 electrodes did not meet the minimum ultimate tensile strength (UTS) requirement. The low silicon content Monel 67 electrode, which does not contain niobium, would not produce weld strengthening niobium silicides and, therefore, was not recommended as the cast niobium modified 70/30 copper nickel welding electrode.

It would be expected that the niobium free electrodes would have poorer resistance to erosion corrosion than the higher strength electrodes. This, however, was not the case. The higher strength 1802 and 1788 samples, welded with niobium containing Cuprotrode 521 electrodes, had poorer erosion corrosion resistance than the 1800 samples.

One characteristic differentiating the niobium modified 70/30 copper nickel parent metal and weld metal from the chromium modified parent metal and the niobium free weld metal respectively, is the presence of niobium silicides. It may be that the presence of niobium silicides has a deleterious effect on the erosion corrosion resistance of 70/30 copper nickel.

It should be noted that the eroded surface of the chromium modified alloy was more textured than the eroded surface of the niobium modified alloy, as illustrated in Figure 33. The chromium modified alloy's dendrites were less susceptible to erosion corrosion than either its interdendritic regions, or the dendrites in the niobium modified alloy.

There is an indication that selective areas such as welds and heat affected zones can be more susceptible to erosion corrosion damage than the surrounding parent metal. It is, therefore, important to consider not only the choice of materials to be used in a firemain system, but also its design and fabrication. The most severe erosion conditions will occur where local turbulence is generated at sharp bends, misaligned joints, partly opened valves, etc. Consideration of joint design will, therefore, be important. It is desirable to have sound, smooth welds with controlled penetration in order to reduce the disruption of smooth flow conditions.

## CONCLUSIONS

1. The erosion corrosion evaluations have shown that cast chromium modified 70/30 copper nickel has greater resistance to erosion corrosion by direct impingement of seawater, entrained with 3.4% air, at 12.2 m/sec, than the more common cast niobium modified 70/30 copper nickel alloy.

2. Under the same severe conditions, welded cast chromium modified 70/30 copper nickel has greater resistance to erosion corrosion than welded cast niobium modified 70/30 copper nickel, but has less resistance than the parent cast chromium modified alloy.

3. Under the same severe conditions, the parent metal of the chromium modified alloy exhibited erosion corrosion resistance that was as good as or better than that of the presently employed firemain materials, but the weld metal of the chromium modified alloy was generally not as resistant.

4. Under the same severe conditions, welds produced in niobium modified 70/30 copper nickel with Monel 67 GMAW electrodes have greater resistance to erosion corrosion than those produced with niobium modified Cuprotrode 521 GMAW electrodes.

5. The temperature of seawater has a significant effect on the susceptibility of copper base alloys to erosion corrosion. The erosion corrosion attack was generally greater when the alloys studied were exposed to temperatures higher than 5°C than when exposed to temperatures lower than 5°C.

6. The results of this erosion corrosion investigation, combined with the results of the castability/weldability studies carried out at Energy, Mines and Resources Canada, indicate that a welded firemain system using the chromium modified 70/30 copper nickel casting alloy could result in a lighter weight and more easily fabricated seawater system.

## TABLE I

## NOMINAL CHEMICAL COMPOSITIONS OF THE ALLOYS

| | Cu | Ni | Fe | Mn | Si | Nb | Cr | Zr | S | Pb | Sn | C | Ti | Zn | P |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| UNS C96400 CAST Nb MODIFIED 70/30 COPPER NICKEL | 65-69 | 28-32 | .25-1.5 | 1.5 MAX | .5 MAX | .5-1.5 | - | - | - | .03 MAX | - | .15 MAX | - | - | - |
| IN 768 CAST Cr MODIFIED 70/30 COPPER NICKEL | BAL | 28-33 | 1.0 MAX | .4-1.0 | .3-.6 | - | 1.4-2.0 | .05-.15 | .02 MAX | .01 MAX | - | .07 MAX | .1 MAX | - | .02 MAX |
| UNS C70600 WROUGHT 90/10 COPPER NICKEL | 86.5 MIN | 9.0-11.0 | 1.0-1.8 | 1.0 MAX | - | - | - | - | - | .05 MAX | - | - | - | 1.0 MAX | - |
| UNS C92200 ASTM B61 LEADED TIN BRONZE | 86-90 | 1.0 MAX | 0.25 MAX | - | .005 MAX | - | - | - | .05 MAX | 1.0-2.0 | 5.5-6.5 | - | - | 3.0-5.0 | .05 MAX |

## TABLE II

## NOMINAL MECHANICAL PROPERTIES OF THE COPPER BASE ALLOYS

| | ULT. TENSILE STRENGTH MPa (Ksi) | YIELD STRENGTH MPa (Ksi) | % ELONGATION |
|---|---|---|---|
| UNS C96400 CAST Nb MODIFIED 70/30 COPPER NICKEL | 415 (60) | 220 (32) | 20 |
| IN 768 CAST Cr MODIFIED 70/30 COPPER NICKEL | 517 (75) | 331 (48) | 18 |
| UNS C70600 WROUGHT 90/10 COPPER NICKEL | 260 (38) | 90 (13) | 30 |
| UNS C92200 CAST ASTM B61 LEADED TIN BRONZE | 235 (34) | 110 (16) | 22 |

## TABLE III

## CHEMICAL COMPOSITION OF GMAW ELECTRODES

| | Cu | Ni | Fe | Mn | Si | Nb | Cr | Zr | S | Pb | C | Ti | Zn | P |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| MONEL 67 * | 68.08 | 30.11 | 0.57 | 0.82 | 0.05 | - | - | - | 0.002 | - | 0.03 | 0.34 | - | - |
| CUPROTRODE 521 ** | 66.93 | 30.72 | 0.51 | 0.79 | 0.40 | 1.02 | - | - | 0.005 | 0.005 | 0.43 | - | 0.009 | - |
| MONEL 451 ** | 66.12 | 30.20 | 0.15 | 2.00 | 0.48 | - | 2.17 | 0.036 | 0.005 | - | <0.02 | 0.09 | - | <0.005 |

* MANUFACTURERS CERTIFIED ANALYSIS

** CANMET WET CHEMICAL ANALYSIS

# TABLE IV

## SUMMARY OF GMA WELDING CONDITIONS FOR Nb MODIFIED SAMPLES

| | 1800 | 1802 | 1788 |
|---|---|---|---|
| electrode | Monel 67 | Cuprotrode 521 | Cuprotrode 521 |
| shielding gas | argon | argon | argon<br>+ 2% $O_2$ |

## TABLE V

## SLOPES AND COEFFICIENTS OF DETERMINATION FROM LINEAR LEAST SQUARES ANALYSIS

| | All Data Points ($mg/cm^2 \cdot hour$) | | Data at < 5°C ($mg/cm^2 \cdot hour$) | | Data at > 5°C ($mg/cm^2 \cdot hour$) | |
|---|---|---|---|---|---|---|
| | Slope | $r^2$ | Slope | $r^2$ | Slope | $r^2$ |
| Cr modified 70/30 copper nickel | 0.042 | 0.35 | 0.030 | 0.90 | 0.062 | 0.67 |
| Nb modified 70/30 copper nickel | 0.061 | 0.16 | 0.044 | 0.44 | 0.087 | 0.63 |
| 90/10 copper nickel | 0.051 | 0.77 | 0.046 | 0.72 | 0.053 | 0.84 |
| ASTM B61 leaded tin bronze | 0.058 | 0.71 | 0.055 | 0.74 | 0.059 | 0.74 |
| welded Cr modified 70/30 copper nickel | 0.076 | 0.70 | 0.031 | 0.86 | 0.091 | 0.82 |
| welded Nb modified 70/30 copper nickel | 0.125 | 0.81 | 0.071 | 0.65 | 0.139 | 0.89 |
| welded 1800 samples | 0.060 | 0.64 | 0.066 | 0.74 | 0.053 | 0.83 |
| welded 1802 samples | 0.133 | 0.88 | 0.078 | 0.68 | 0.143 | 0.97 |
| welded 1788 samples | 0.139 | 0.86 | 0.066 | 0.97 | 0.153 | 0.96 |

$r^2$ = coefficient of determination

when $r^2 = 1$ exact correlation
when $r^2 = 0$ uncorrelated

# TABLE VI

## MAXIMUM DEPTH OF ATTACK AFTER 1644 HOURS OF EXPOSURE

| Sample | Max. depth of attack (mm) | Location |
|---|---|---|
| Cr modified 70/30 copper nickel | 0.46 | weld metal |
| Nb modified 70/30 copper nickel (1802 and 1788 samples) | 0.86 | weld metal |
| Nb modified 70/30 copper nickel (1802 and 1788 samples) | 1.45 | HAZ |

# TABLE VII

## ELECTRON PROBE MICROANALYSIS OF WELDED CHROMIUM AND NIOBIUM MODIFIED 70/30 COPPER NICKEL

| Alloy | Surface | Location | % Cu | % Ni |
|---|---|---|---|---|
| Cr | eroded | peaks | 55 | 42 |
| Cr | eroded | valleys | 70 | 27 |
| Cr | polished/etched | dendrites | 56 | 39 |
| Cr | polished/etched | interdendrites | 74 | 24 |
| Nb | eroded | peaks | 61 | 36 |
| Nb | eroded | valleys | 72 | 25 |
| Nb | polished/etched | dendrites | 57 | 37 |
| Nb | polished/etched | interdendrites | 80 | 19 |

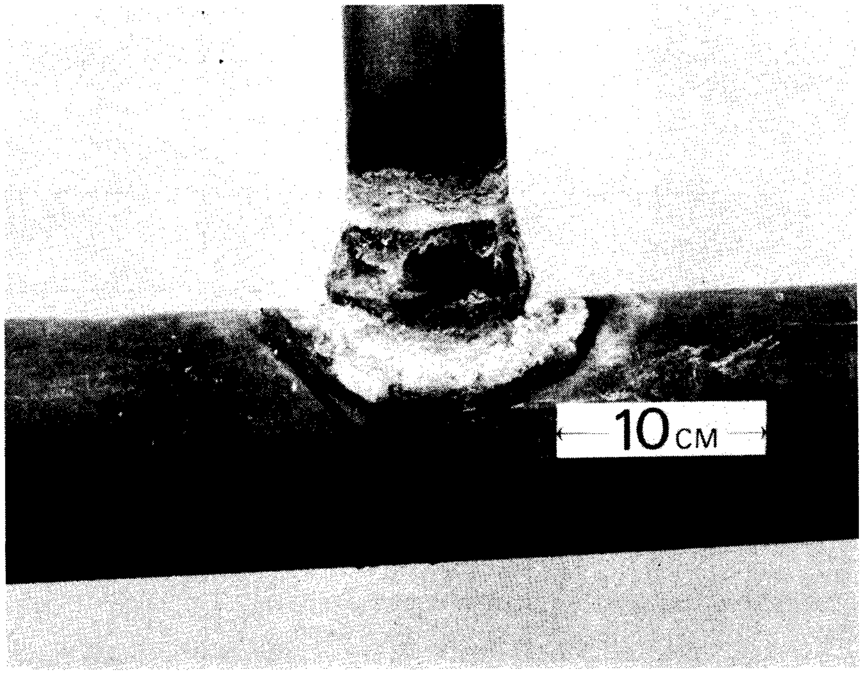

Figure 1: Method of fabricating a 90° joint using a brazolet.

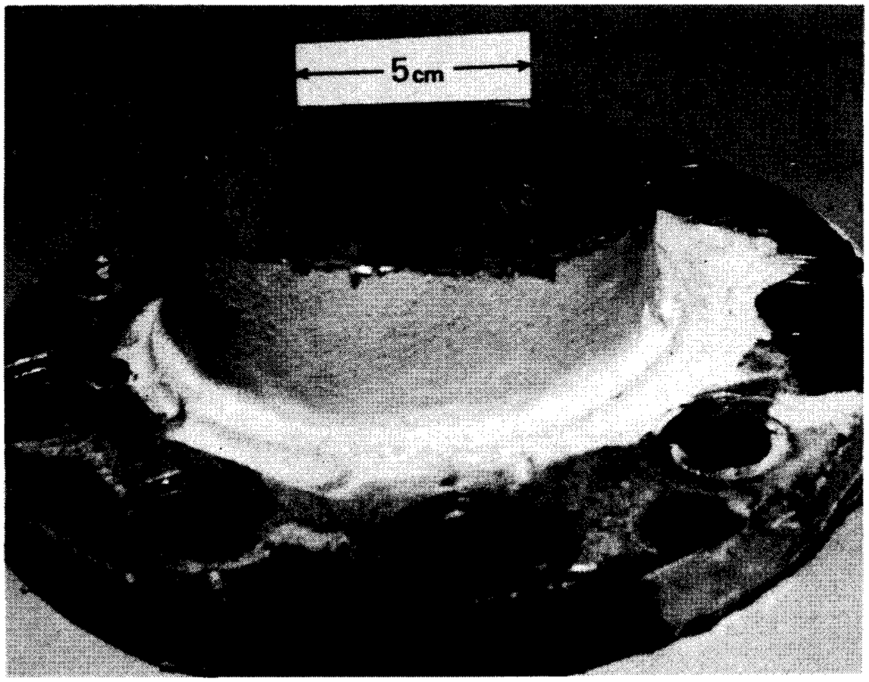

Figure 2: Cracking of copper nickel pipe caused by liquid metal embrittlement.

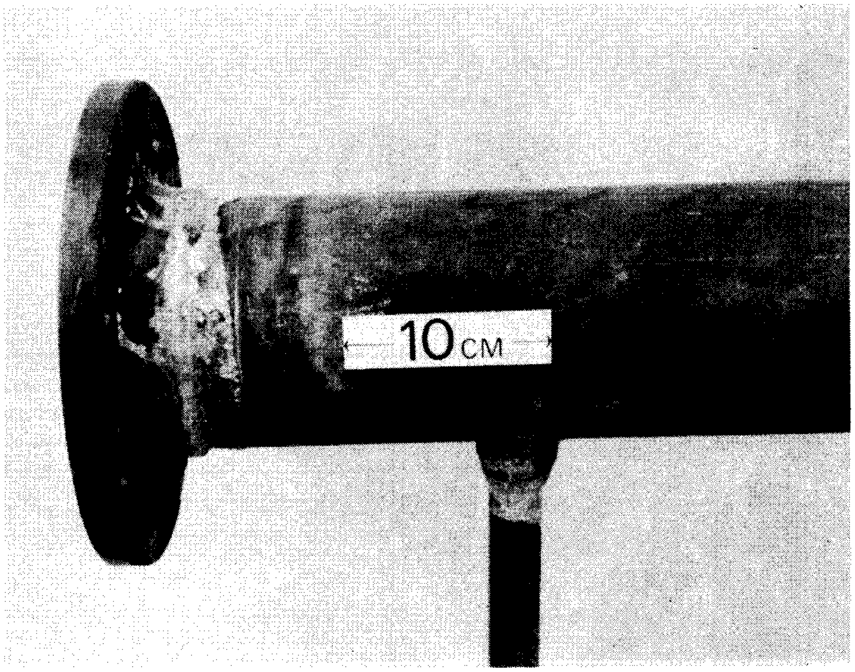

Figure 3: Silver brazed flange/pipe joint.

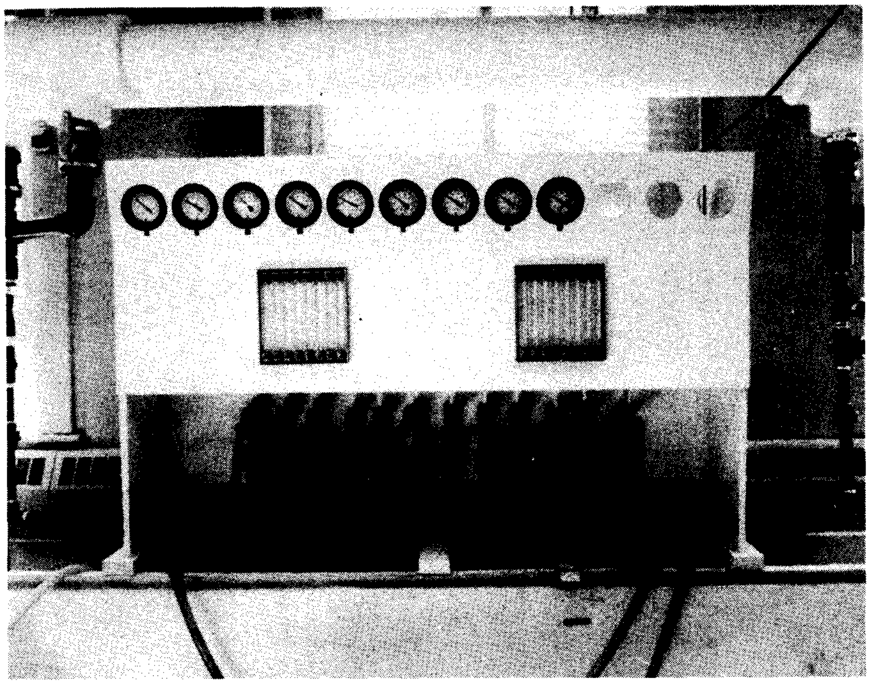

Figure 4: Jet impingement test apparatus.

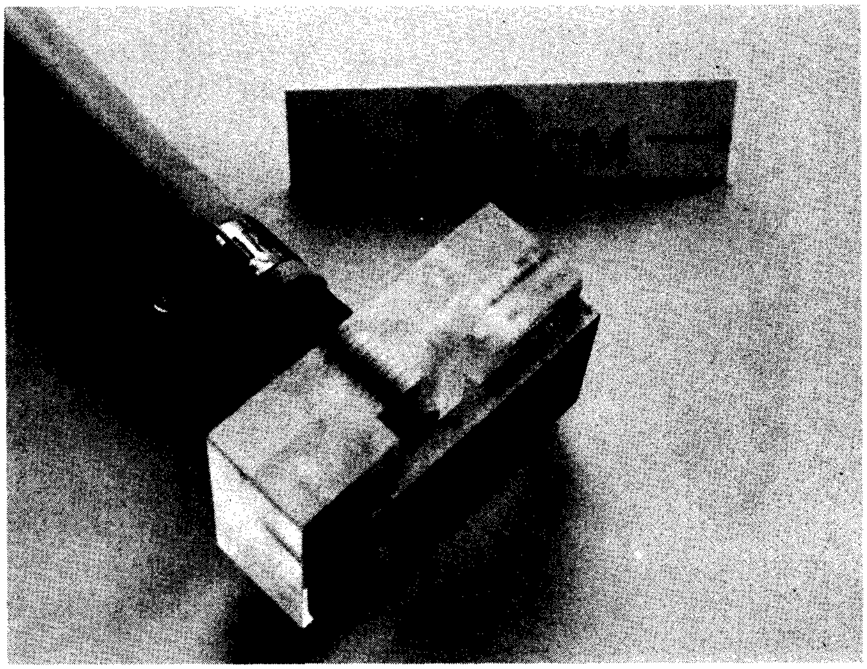

Figure 5: Sample holder.

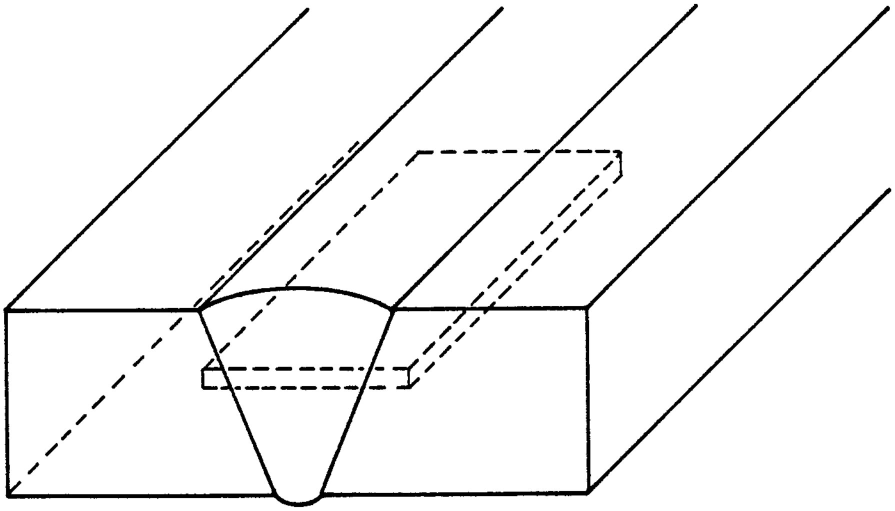

Figure 6a: Weld metal sample.

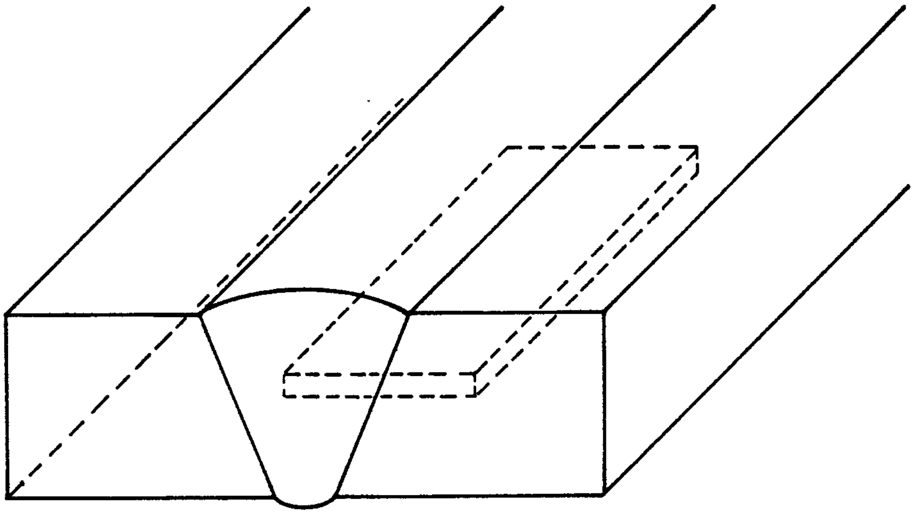

Figure 6b: HAZ samples.

Figures 6a & 6b: Location of samples within welded bars.

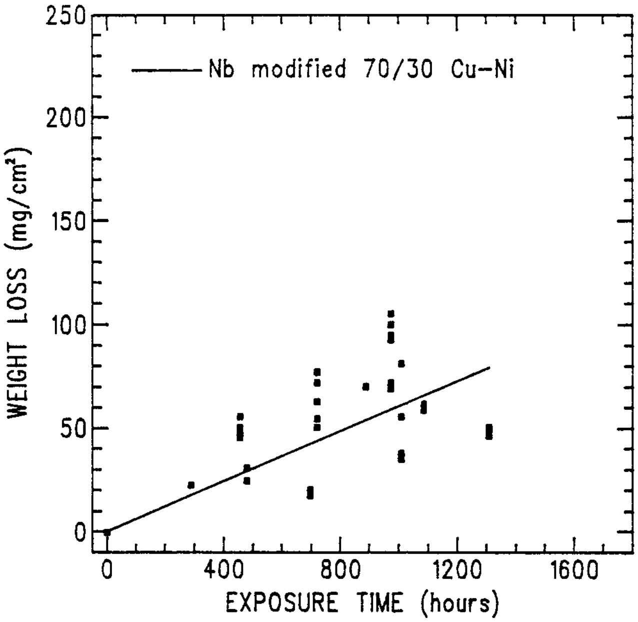

Figure 7: Results of jet impingement tests on as-cast niobium modified 70/30 copper nickel, using all data.

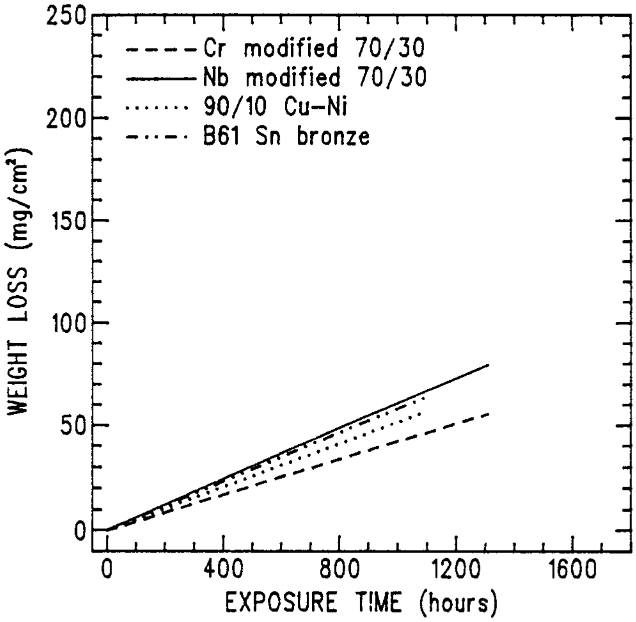

Figure 8: Results of jet impingement tests on parent metal samples, using all data.

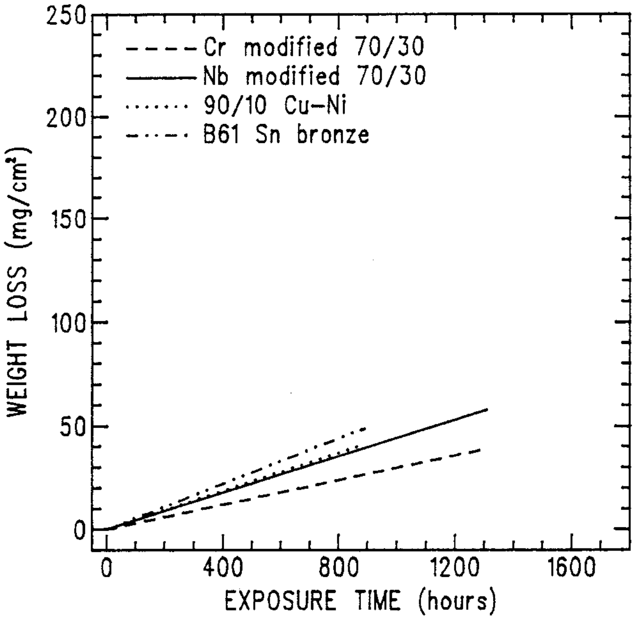

Figure 9: Results of jet impingement tests on parent metal samples, using data at temperatures lower than 5°C.

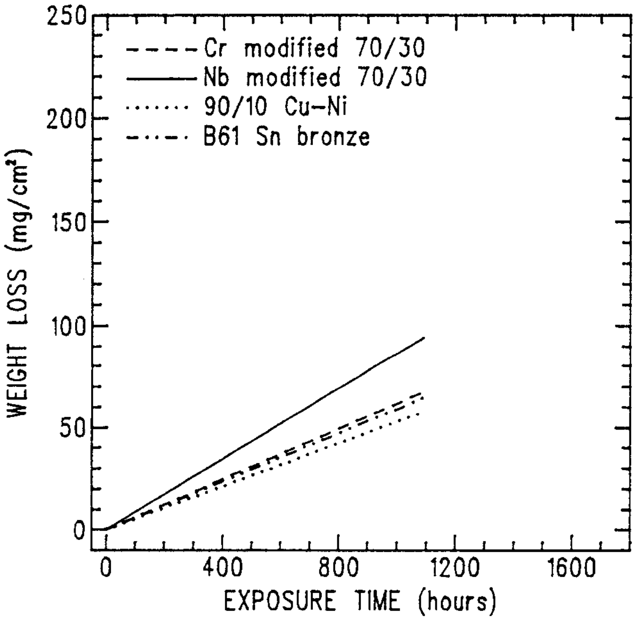

Figure 10: Results of jet impingement tests on parent metal samples, using data at temperatures higher than 5°C.

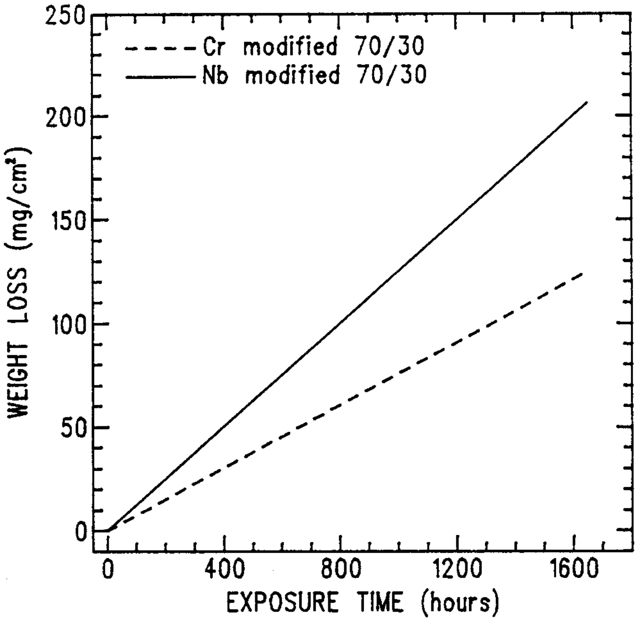

Figure 11: Results of jet impingement tests on weld metal samples, using all data.

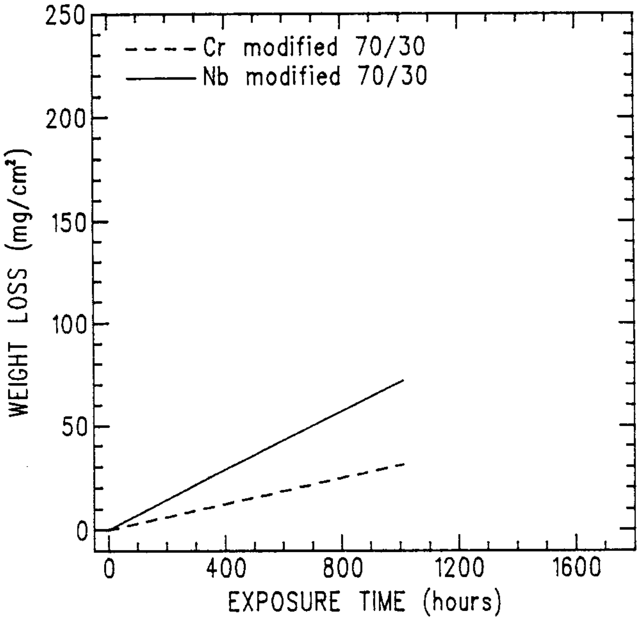

Figure 12: Results of jet impingement tests on weld metal samples, using data at temperatures lower than 5°C.

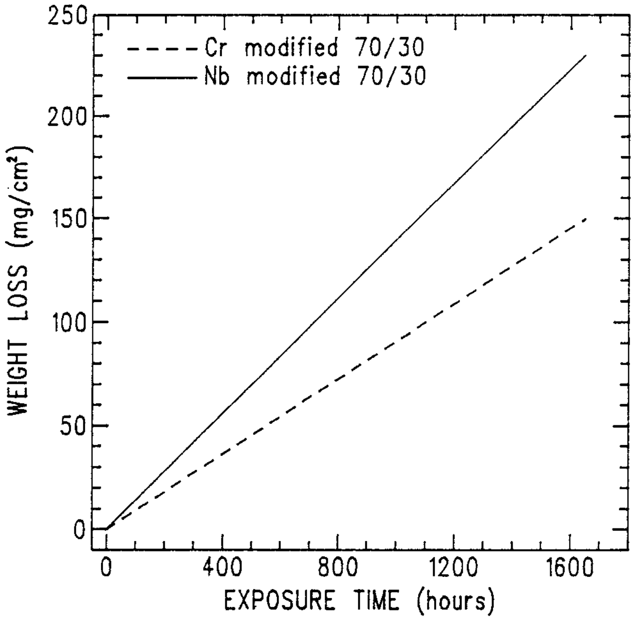

Figure 13: Results of jet impingement tests on weld metal samples, using data at temperatures higher than 5°C.

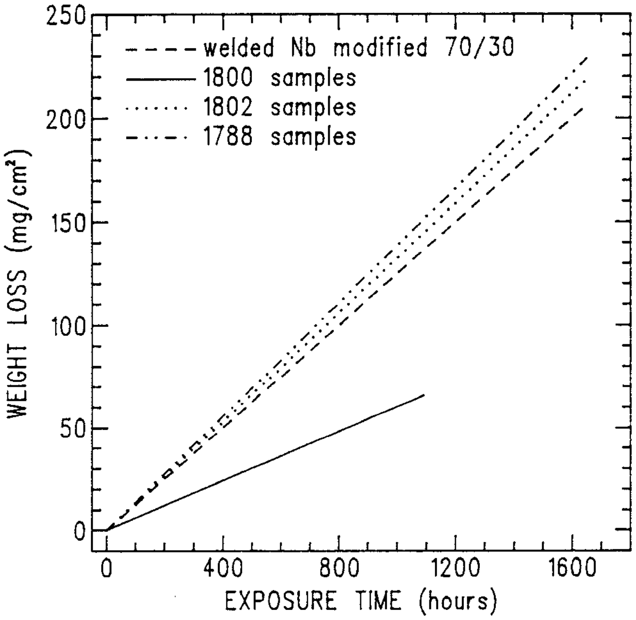

Figure 14: Comparison of three sets of niobium modified 70/30 copper nickel, welded under different conditions as outlined in Table IV, using all data.

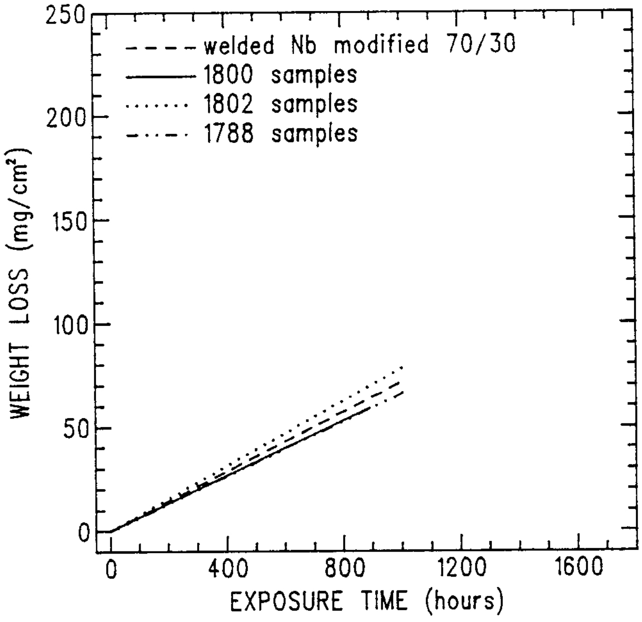

Figure 15: Comparison of three sets of welded niobium modified 70/30 copper nickel, using data at temperatures lower than 5°C.

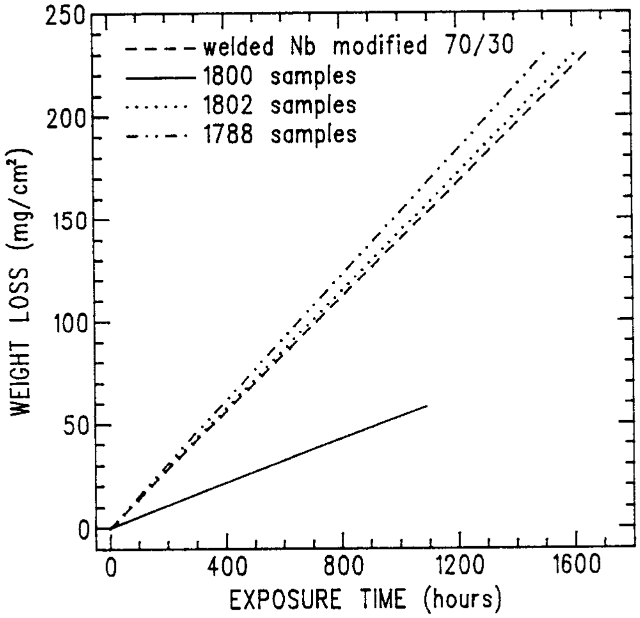

Figure 16: Comparison of three sets of welded niobium modified 70/30 copper nickel, using data at temperatures higher than 5°C.

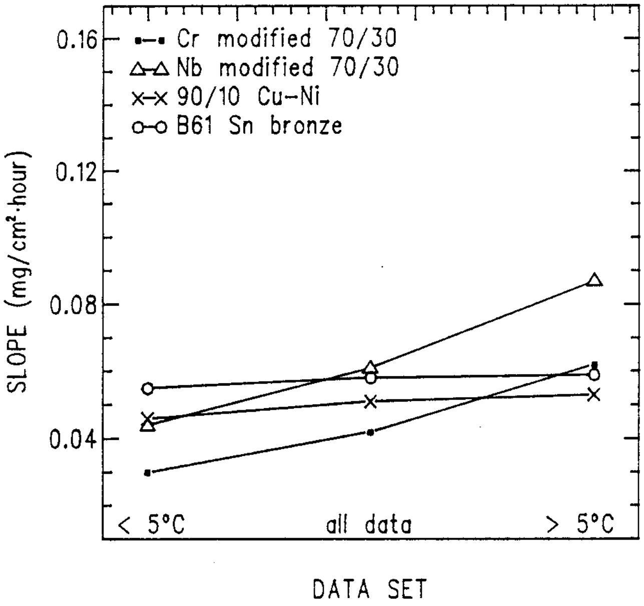

Figure 17: Slopes from linear least squares analysis of parent metal data.

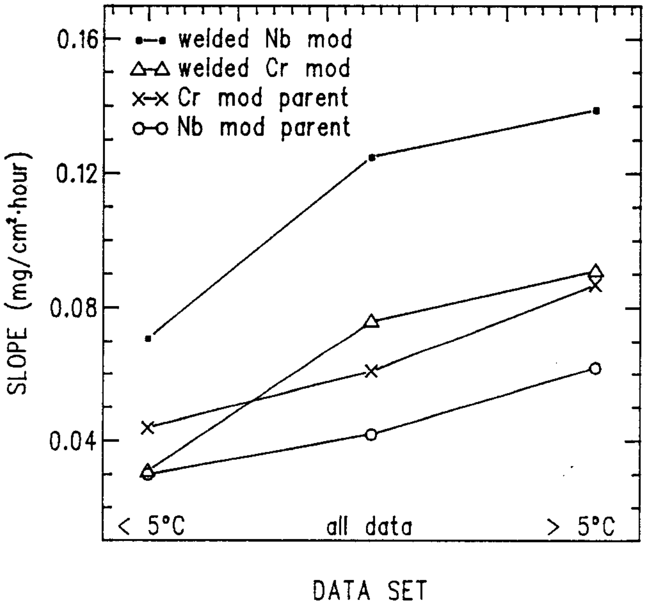

Figure 18: Slopes from linear least squares analysis of welded and as-cast 70/30 copper nickel data.

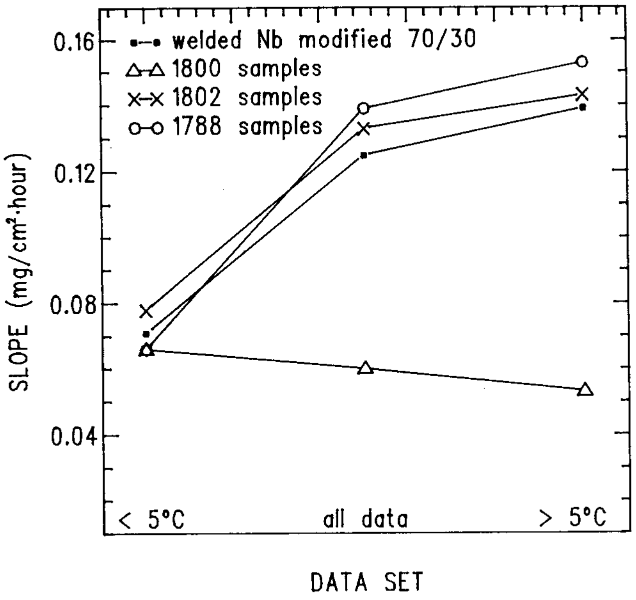

Figure 19: Slopes from linear least squares analysis of niobium modified 70/30 copper nickel, welded under different conditions as outlined in Table IV.

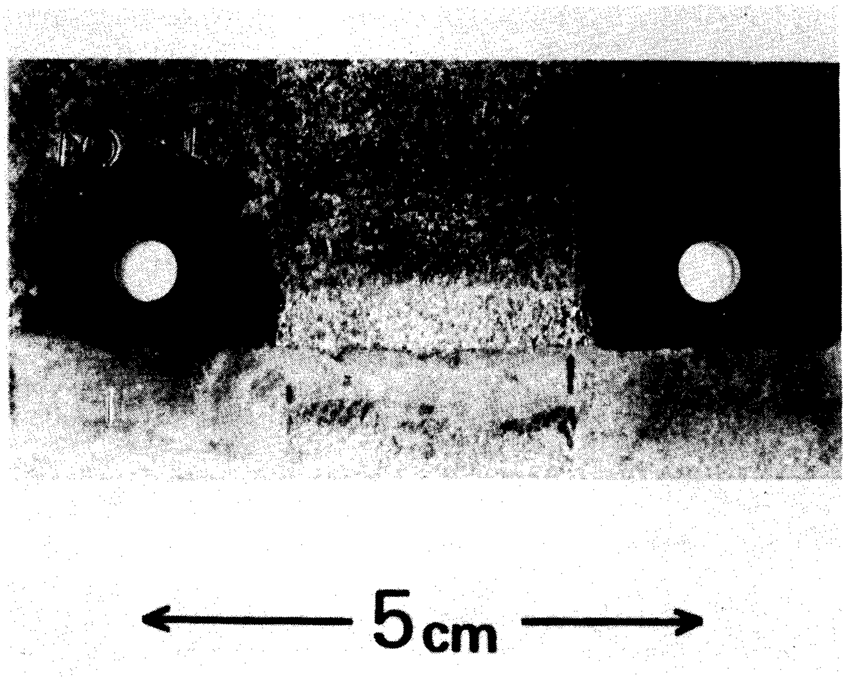

Figure 20: Welded chromium modified 70/30 copper nickel sample showing erosion after 1644 hours exposure to jet impingement.

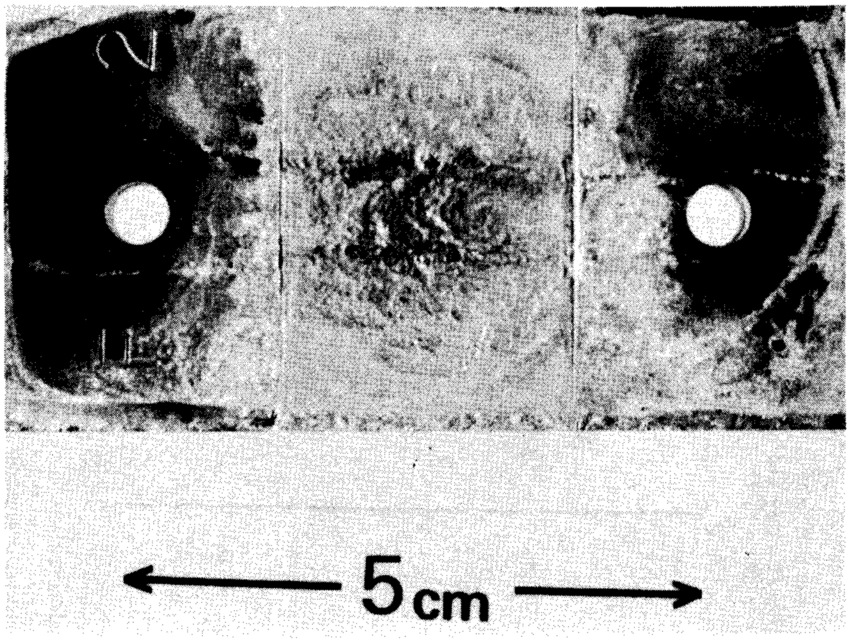

Figure 21: Welded niobium modified 70/30 copper nickel sample showing attack along weld pass interfaces after 1644 hours exposure.

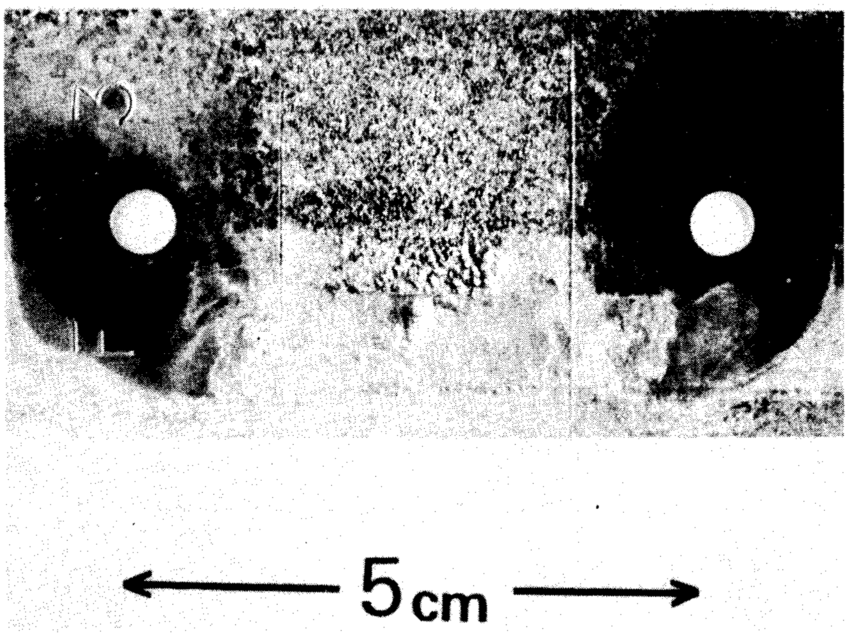

Figure 22: Welded niobium modified 70/30 copper nickel sample showing greater depths of attack within HAZ in centre of sample.

Figure 23: Chromium modified 70/30 copper nickel alloy welded with Monel 451 electrodes (parent metal on right). Alcoholic ferric chloride etch. (X30)

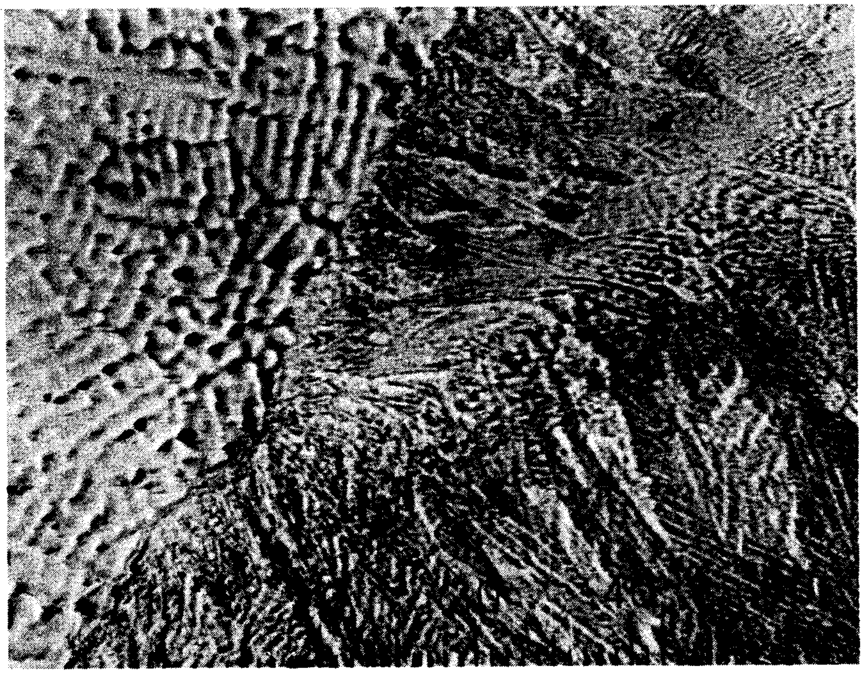

Figure 24: Niobium modified 70/30 copper nickel alloy welded with Cuprotrode 521 electrodes (parent metal on left). Alcoholic ferric chloride etch. (X30)

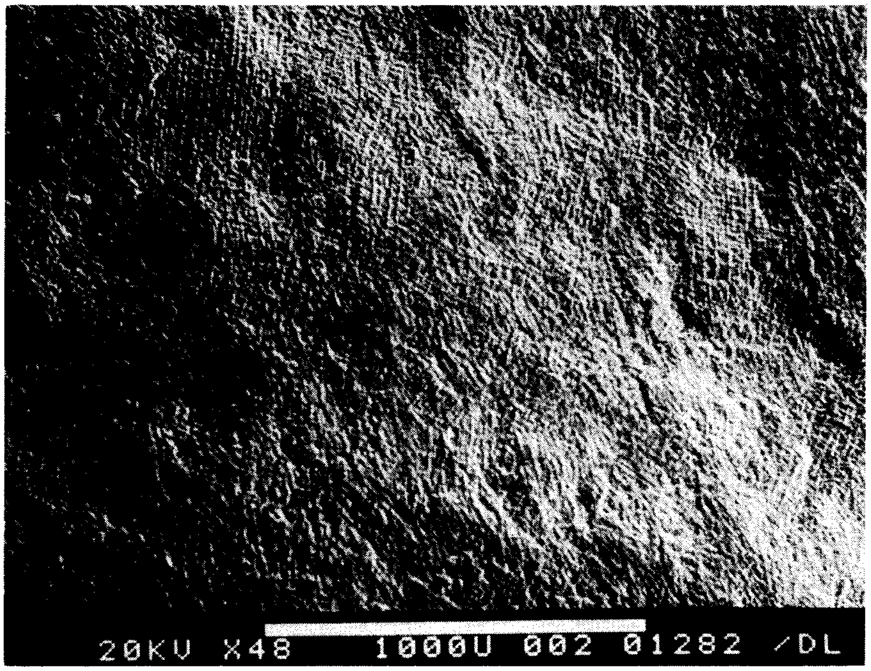

Figure 25: Eroded surface of niobium modified 70/30 copper nickel alloy weld metal (Cuprotrode 521). (X48)

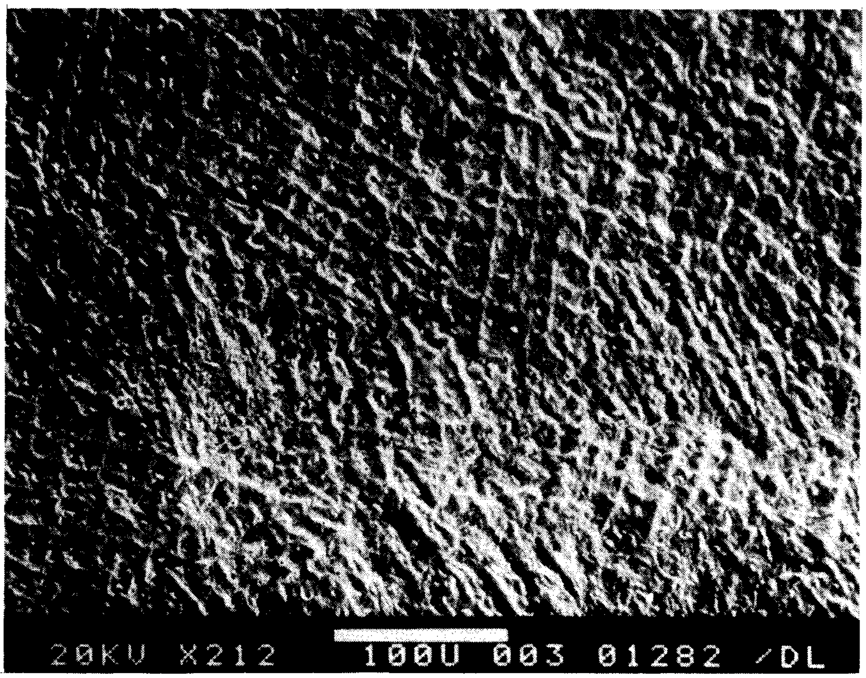

Figure 26: Eroded surface of niobium modified 70/30 copper nickel alloy weld metal (Cuprotrode 521). (X212)

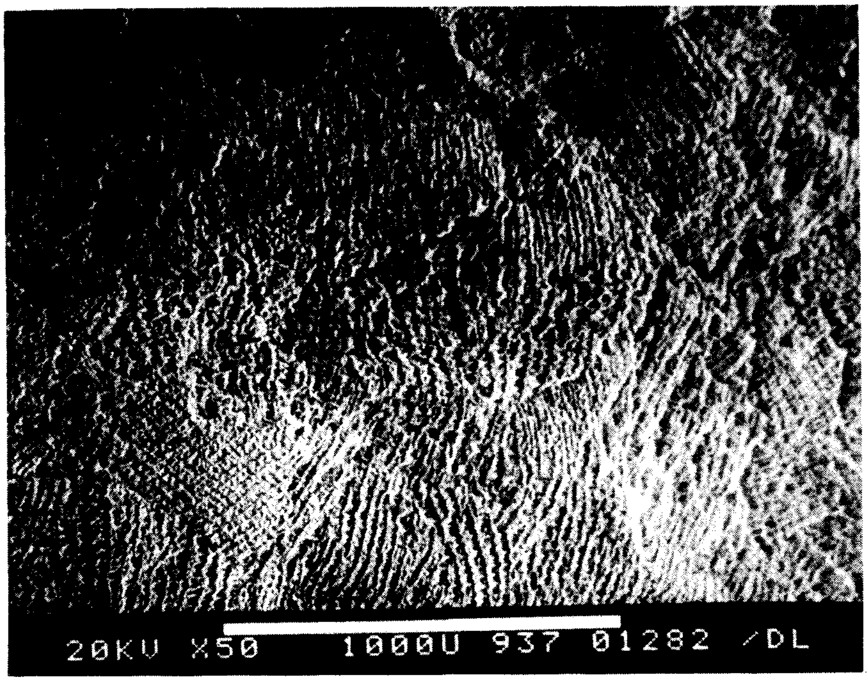

Figure 27: Eroded surface of chromium modified 70/30 copper nickel weld metal (Monel 451). (X50)

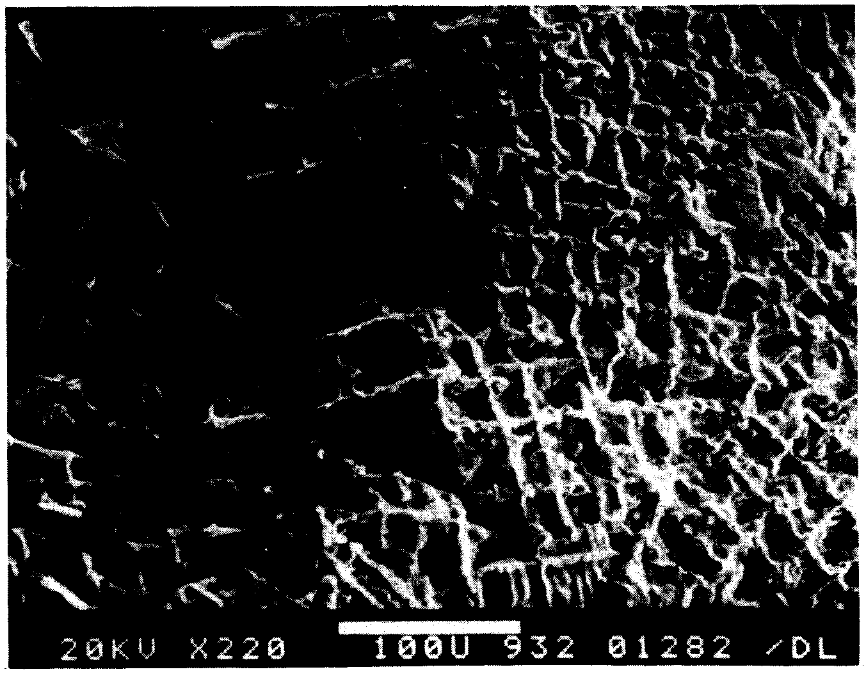

Figure 28: Eroded surface of chromium modified 70/30 copper nickel weld metal (Monel 451). (X220)

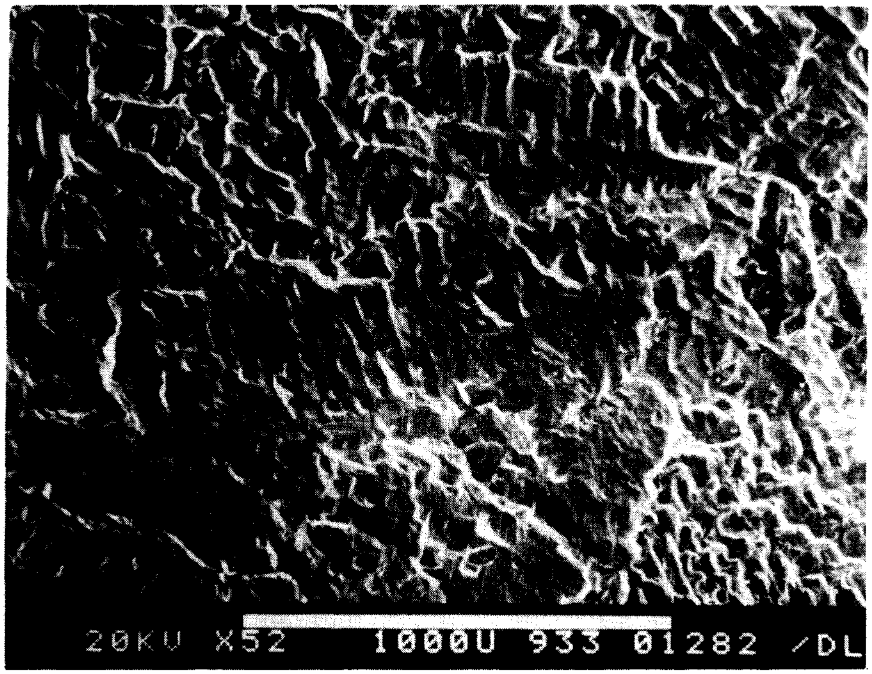

Figure 29: Eroded surface of chromium modified 70/30 copper nickel alloy parent metal. (X52)

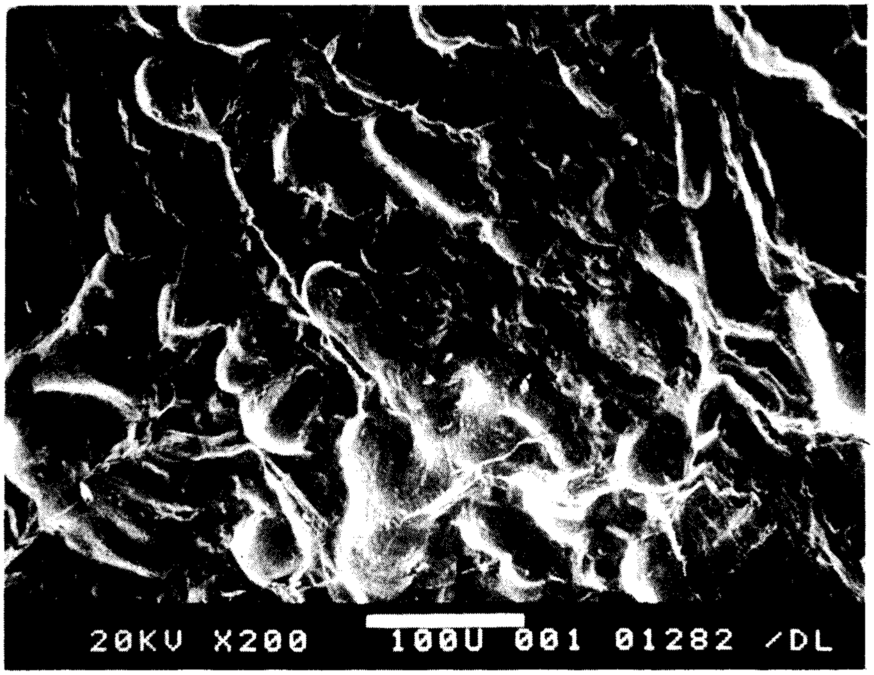

Figure 30: Eroded surface of chromium modified 70/30 copper nickel alloy parent metal. (X200)

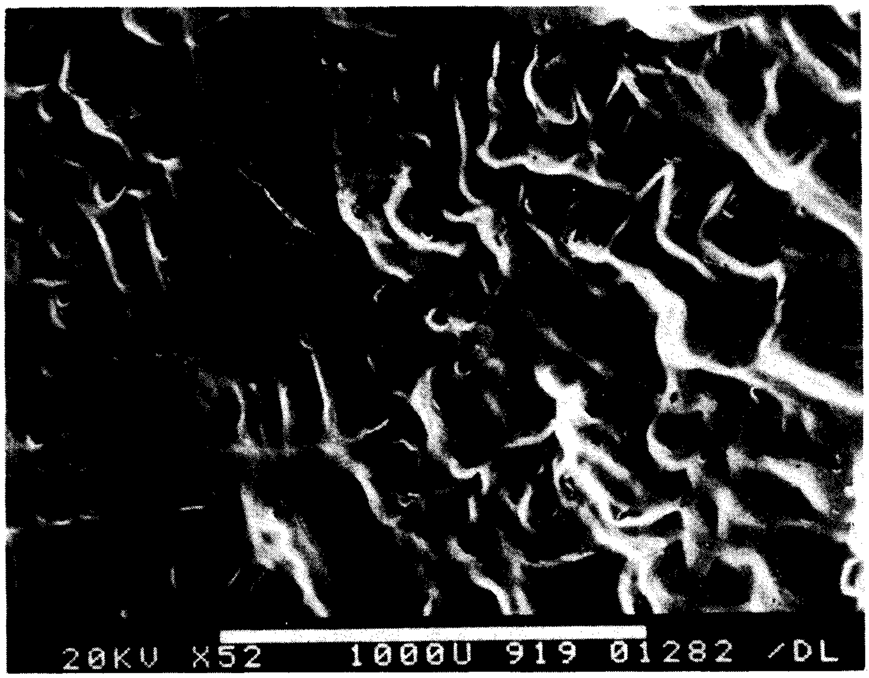

Figure 31: Eroded surface of niobium modified 70/30 copper nickel alloy parent metal. (X52)

Figure 32: Eroded surface of niobium modified 70/30 copper nickel alloy parent metal. (X204)

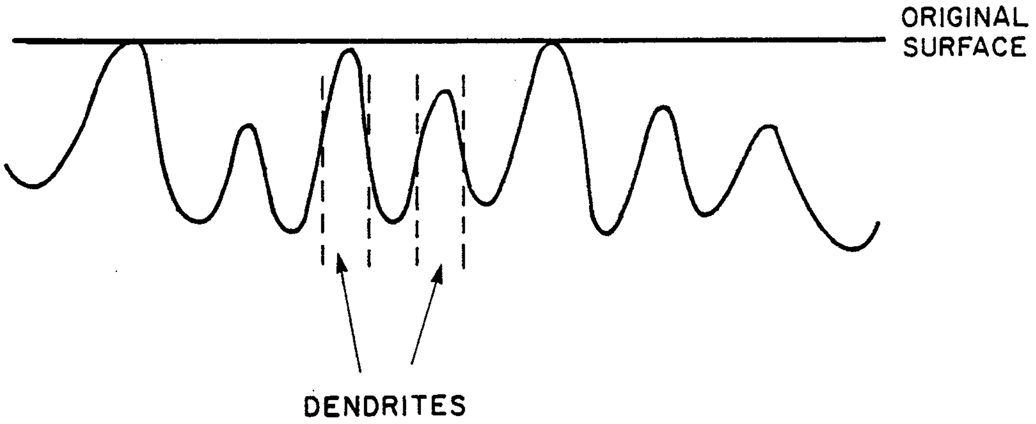

Figure 33 (a)

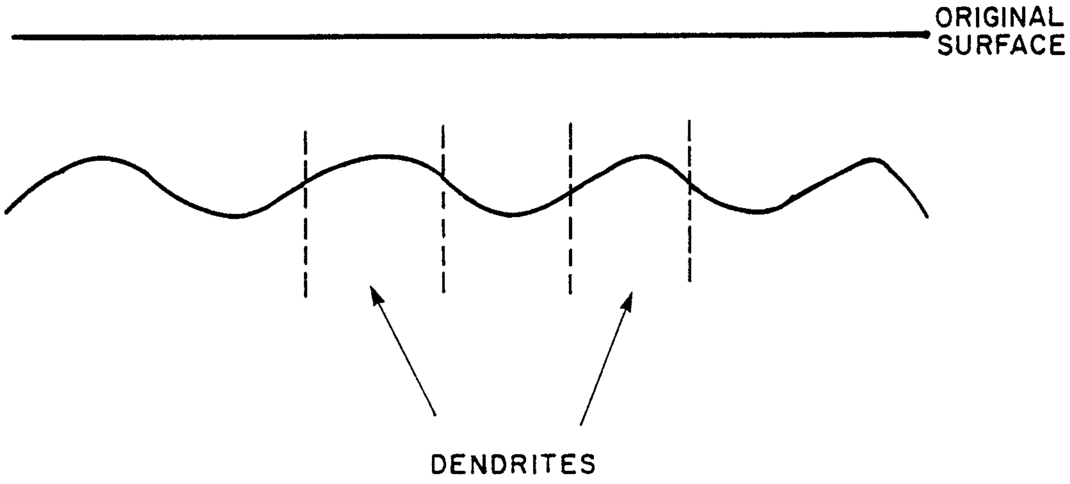

Figure 33 (b)

Figures 33a & 33b: Schematic of the eroded surface of the (a) chromium modified, and (b) niobium modified copper nickel alloy.

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13. ABSTRACT

The firemain system on Canadian warships was designed to be fabricated by silver brazing. Over the past number of years, some difficulties have been encountered when employing the brazing technique. To overcome these difficulties it is being proposed that the firemains on the new ships be of an all welded construction. An additional benefit will be a reduction in the overall weight of the firemain system. The erosion corrosion resistances of two potential replacement weldable alloys with sufficient strength were evaluated: cast chromium modified 70/30 copper nickel and cast niobium modified 70/30 copper nickel. For comparison purposes the present firemain materials, wrought 90/10 copper nickel and cast leaded tin bronze (ASTM B61), were also tested. The weight loss of the alloys was measured after exposure to impingement attack by seawater jets mixed with air bubbles. Cast chromium modified 70/30 copper nickel in both the welded and parent metal conditions had greater resistance to erosion corrosion under the severe conditions to which the alloys were exposed than the niobium modified alloy. The parent metal of the chromium modified alloy exhibited erosion corrosion resistance that was as good as or better than that of the presently employed materials, but the weld metal of the chromium modified alloy was generally not as resistant.

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seawater

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jet impingement

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