THE INSTITUTE OF MARINE ENGINEERS
*76 Mark Lane, London EC3R 7JN* *Telephone: 01-481 8493 Telex: 886841*

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# NEW MATERIALS FOR THE MARINE AND OFFSHORE INDUSTRY

J. F. G. Condé

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# New Materials for the Marine and Offshore Industry

**J. F. G. Condé**
Admiralty Research Establishment, Holton Heath

## SYNOPSIS

*The history of materials usage in the marine and offshore industry is surveyed briefly and the factors which have led to their application are indicated. The current introduction of new materials into structural applications and engineering systems is described and potential near term and longer term use of new metallic, organic and ceramic materials is discussed together with technical and economic benefits which may accrue.*

### INTRODUCTION

Portland cement is one of a select group of older established materials which were developed in the first instance specifically for use in marine applications. Developed by Smeaton in 1756 as a jointing material for the Eddystone lighthouse, it has subsequently found more extensive application on land than in the marine industry. In contrast, other materials, such as copper, were produced for non-marine applications and were later found to have special attributes in marine use.

In this paper, new materials for the marine and offshore industry will be considered to comprise both classes of materials and to embrace not only those developed to overcome some specific shortcomings in properties which accompany or inhibit the use of existing materials but also those intended for land based or other uses and found to be endowed with attractive properties in the marine environment.

Mr J. F. G. Condé, BSc, CEng, FIM, studied metallurgy at the University of Wales, Cardiff, and spent several years in industry engaged in research on nickel alloys, subsequently joining the Royal Naval Scientific Service to conduct research on precision fire control equipment. He then joined the UKAEA and was responsible for the successful development of the AGR canning steel and a wide range of materials R & D connected with the OECD 'Dragon' high temperature reactor. In his present post as Head of Metallurgy and Ceramics Division, Admiralty Research Establishment, he is responsible for research on metallurgy and ceramics for the Royal Navy and some triservice activities on ceramics. He was a member of the Department of Industry Corrosion Committee and is currently a member of the DOTI Industrial Advisory Committee on Fracture Avoidance and of The Research Board of The Welding Institute.

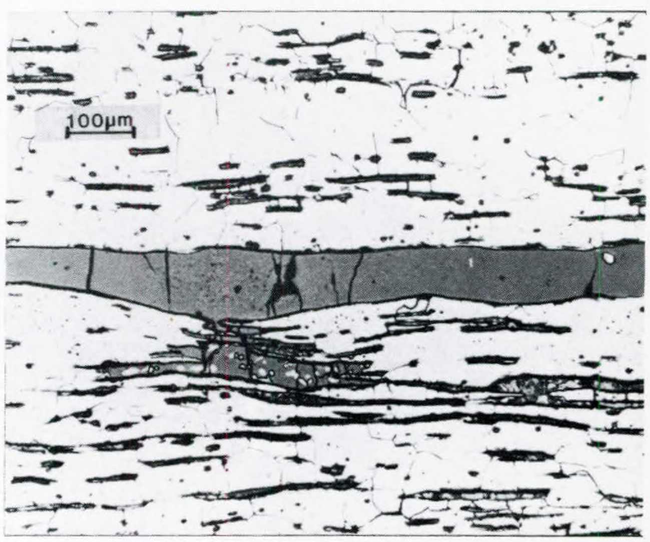
### HISTORICAL BACKGROUND

Wood is undoubtedly the oldest established material for marine applications. Employed because it occurs naturally, it is light and buoyant and can be shaped and fabricated with readily available tools and handling techniques. By the seventeenth and eighteenth centuries, shipyards were the largest manufacturing units then in existence and men-of-war were certainly the largest items in regular manufacture. At that time the hulls of British and French ships were made of oak, with pine for masts and yards. Spanish ships employed mahogany for hulls and decks since it was more resistant to dry rot and Spain had access to the timbers of Cuba and Honduras, many large Spanish ships being constructed at that time in Havana.[1] Nails to secure timber were of oak or mahogany, wrought iron, copper or bronze. Wrought iron bolts of up to nearly 2 metres in length were used with wrought iron or wooden nuts.

Whilst cannon used in ships were of copper alloy, bronzes or cast iron, the first extensive use of metal in ships was early in the seventeenth century, when wooden junks in eastern waters were sheathed with copper to provide protection from the large wood boring worm *Teredo navalis* which exists in tropical seas. Copper sheathing or 'coppering' did not spread to Europe until more than 100 years later, the first recorded application being in the British Navy in 1761 when a trial was carried out on the frigate HMS *Alarm* as an 'experiment of preserving it against the worm'.[2–4]

Iron ships first appeared about 1822 and iron was supplanted by steel in the last quarter of the nineteenth century. Warship designers in most maritime countries had been reluctant to build unarmoured ships with iron hulls because of the splinters produced when an iron plate was hit by a solid shot. However, a number of iron warships were built and a few saw action but perhaps fortunately in warm climates, since the wrought iron was quite brittle under moderately cold conditions.

**FIG. 1: Microstructure of wrought iron hull plating from HMS *Warrior***



A recent study of material from the hull of HMS *Warrior*[5] which was the first of the line of RN iron hulled, armourclad, ships has proved informative and Figs 1 and 2 show the microstructure of the approximately 12.5 mm thick hull plating and a macrograph of a T frame respectively. The mechanical properties of the hull plating and 100 mm thick armour plating are shown in Table I.

The importance of toughness and resistance to crack propagation in steels for hulls first became clearly apparent when all-welded construction was widely adopted in World War II and some spectacular failures occurred. Between 1942 and 1952, more than 200 ships had sustained serious fractures and at least nine T-2 tankers and seven Liberty ships had broken completely in two. Although such failures generally originated from bad design details or poor welding practice, they led to the development of the carbon manganese class of steels with improved resistance to brittle or fast fracture and better crack arrest properties.

The exploitation of offshore gas and oil supplies initially in areas such as the Gulf of Mexico led to the erection of several thousand steel structures. These were mainly of the welded tubular steel space-frame type, piled to the seabed and in relatively calm waters rarely deeper than 60 metres.[6] Steel used generally conformed to ASTM A36—a weldable steel for general structural purposes (tensile strength 400/500 N/mm$^2$; yield point 248 N/mm$^2$). Similar platforms were employed for extraction of gas from the southern area of the North Sea subsequent to its discovery in 1965. These demonstrated that they were in certain instances under-designed to withstand the more onerous environment in the North Sea and some had to be strengthened. The need to exploit oil in the northern and deeper areas of the North Sea in the early 1970s also imposed the requirement to withstand higher wind speeds and larger waves than had been catered for in any previous offshore steel structures.

Significant requirements for the primary structural components of deep water production platforms include medium yield strength, good weldability and resistance to fracture and corrosion fatigue in the seawater environment. These were

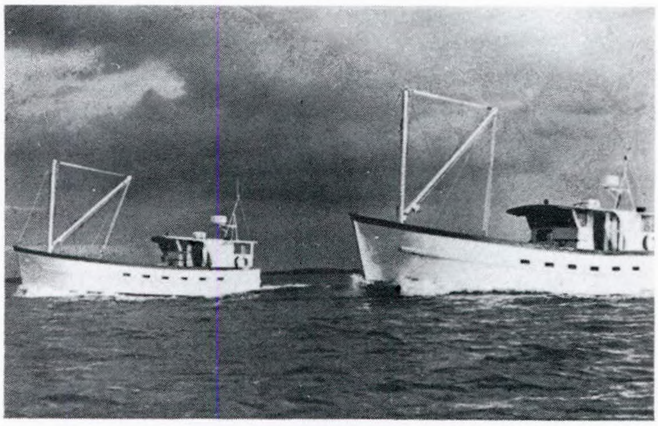


FIG. 3: Small boats with ferrocement hulls[8]

met by weldable structural steels conforming to BS 4360, which embraces materials with yield strengths ranging from 210 to 450 N/mm$^2$. The majority of the steel used was to Grade 50D with a minimum yield strength of 340 N/mm$^2$ and Charpy Vee notch values of 41J at −20°C; 27J at −30°C. These steels are carbon manganese steels, silicon killed and grain refined with niobium and/or vanadium or aluminium and controlled low carbon levels to ensure good weldability. Some limited use has also been made of Grades 43E and 55E (250; 415 N/mm$^2$ YS).

Naturally occurring rock and natural cements have been used extensively in fixed marine structures and sea defences. The high durability of concrete employing natural cements was instrumental in its use by the Egyptians and Romans for harbours and breakwaters. Following the development of Portland cement in the eighteenth century a Frenchman, Lambot, constructed two small boats in 1848 and 1849 by applying a sand–cement mortar mix over a framework of iron bars and mesh.[7] These small craft were the first examples of ferrocement construction and established the principles still in use today.

The use of ferrocement concrete hulls was boosted in the two world wars by the need to save steel and to make use of comparatively unskilled labour. In more recent times ferrocement construction for hulls has been utilized in China and South East Asia. Figure 3 shows examples of small boats with ferrocement hulls. Reinforced concrete for hull construction was first adoped in 1897 in Italy and widely used in World War I for barges and larger seagoing vessels, the largest of these being built in the USA (6340 t and 130 m length). World War II saw the construction of a variety of barges and other seagoing structures, including floating docks and the Mulberry Harbour pontoons. Prestressed concrete was first used in Germany in 1943 for construction of 500 t barges and in general since World War II this material has been favoured for concrete vessels over about 2000 t deadweight.

In recent years very large oil production platforms built of reinforced and prestressed concrete have been constructed for use in the North Sea (Fig. 4). These are among the largest structures ever built, weighing about ten times more than a steel platform; they are not piled but are gravity structures resting on the seabed. Some 15 such structures are already in place in the North Sea and a further two are under construction; the largest approaches 10$^6$ tonnes in weight. In general, concrete platforms contain at least as much steel (as reinforcement and prestressing tendons) as comparable steel platforms.[6,8]

While the use of natural polymeric materials such as rubber has been commonplace for many years, it was not until the 1950s that glass reinforced plastic (GRP) materials came into use, initially in small boat hulls. The first large scale GRP hulled vessel was the minehunter HMS *Wilton*, built for the Royal Navy some 12 years ago and launched in January 1972.[9]

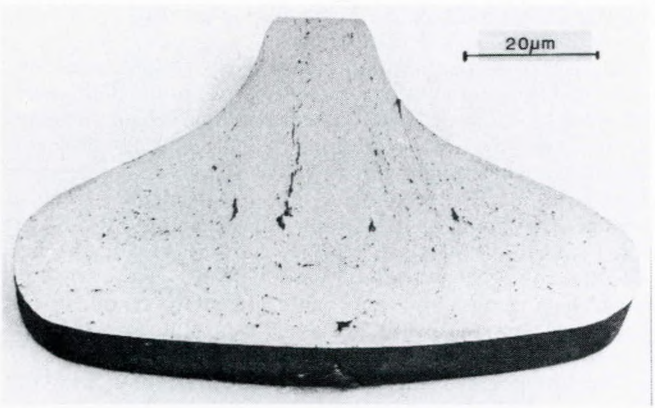



FIG. 2: Macrostructure of wrought iron Tee frame from HMS *Warrior*

**Table I: Properties of wrought iron from hull of HMS Warrior[5]**

| Thickness (mm) | 0.2% Proof stress (N/mm$^2$) | Tensile strength (N/mm$^2$) | Elongation (%) | Reduction of area (%) | Charpy Vee Notch at +15°C (J) |
|---|---|---|---|---|---|
| 12.5 | 220 | 284 | 11 | 1 | 17 |
| 12.5 | 212 | 253 | 8 | 2 | — |
| 100-Surface | 134 | 150 | 6 | 2 | — |
| 100-Centre | 123 | 135 | 5 | 2 | — |

**FIG. 4: Concrete platform for the North Sea[8]**

HMS *Wilton* is 46.6 m LOA × 8.5 m beam, 6.1 m deep and of 465 tonnes displacement; the total weight of GRP is about 132 tonnes. More recently, in December 1979, HMS *Brecon*, the first of a larger class of GRP hulled mine countermeasures vessels (MCMVs), was completed.[10] These are 60 m LOA × 10 m beam, with a mean draught of 2.5 m and a standard displacement of 625 tonnes. They replace a class of minehunters with double mahogany, aluminium framed hulls.

Many other materials have been employed in offshore engineering and in ship main propulsion and auxiliary systems, propellers etc. These include cast iron, steels and copper base alloys for valves and pumps, galvanized steel and copper alloy tubes for seawater systems and a range of brasses and cupronickel alloys for condenser tubes and tube plates. Propellers have employed cast iron, high tensile brasses, various aluminium bronzes and stainless steels. Use has also been made of aluminium and aluminium alloys for superstructures and for the hulls of small craft. Marine gas turbines have employed a wide range of materials, including high strength stainless steels and titanium alloys for compressor blading and nickel base superalloys for combustion systems, nozzle guide vanes and turbine stator and rotor blade materials.

## NEW MATERIALS—GENERAL

The incentives to develop new materials or to use existing materials in radically different applications or environments can be motivated by a variety of driving forces. These include improvement of performance, cost reduction, competition, replacement of scarce or toxic materials, safety and environmental legislation.

New materials are frequently at a disadvantage in cost terms when research and development costs, costs of introduction and routine manufacture are considered in isolation from performance benefits and through-life costs or cost of ownership, which may be difficult to quantify precisely at the decision stage.

Often the need to match design and manufacturing technology to the new material and not to make 'Chinese copies' is not fully appreciated and problems may arise in design, fabrication or use and incur cost penalties. Equally it is not always appreciated that current welding techniques for steels were developed to suit fabrication of steels contemporary with the process development. The newer steels, as will be discussed later, may require different welding processes or techniques in order to achieve the full potential design advantages of the materials.

## FERROUS METALS

In the 1970s and 1980s, the exploitation of offshore energy resources has provided the main incentive for improvements in steel properties. In 1975 offshore exploitation accounted for 15% of the world-wide primary energy production;[12] this rose to 22% by 1980 and is predicted to reach 30% by 1990. Currently there are about 3600[11] offshore platforms worldwide and it is anticipated that by the end of 1985 this will rise to nearly 4000, the vast majority being of steel. Paradoxically, the high cost of oil since 1973 has also promoted attempts in the steel industry to achieve efficiency and cost reduction by automation and energy saving. Improved steel product yields and reduced energy consumption have resulted. The North Sea now accounts for a significant proportion of sales of structural steel products.

During the period since 1950, water depths for offshore platforms have increased from about 20 m to in excess of 300 m and requirements are likely to increase to 500 m or more in future. In general terms, 1 tonne above water requires approximately 10 tonnes of underwater structure and hence there is a considerable incentive to use stronger materials, particularly in deeper waters. Similarly with pipelines, there is an increasing need for larger pipelines to handle higher flows at the same pressure as with smaller diameters.

Up to the present time, for most fixed offshore platforms steel yield strengths have been limited to around 350 $N/mm^2$ (e.g. BS 4360, Grade 50D).[13] This is based on fatigue considerations, the fatigue strength of welds being substantially unaffected by yield strength. An alternative view[14] is that designer familiarity may be the principal reason for selecting steels of around 350 $N/mm^2$ yield strength, since perhaps only 20% of fixed structure nodes are subject to severe fatigue loading. Clearly any steel proposed for use in the severe offshore environment must have appropriate strength combined with toughness, low anisotropy and good through thickness properties (to avoid lamellar tearing) and possess good weldability.

Improvements in steels in the past decade have come about through advances in steel technology coupled with enhanced understanding of metallurgical structure/property relationships and the interplay between alloy additions, processing and thermomechanical treatments.[15] To obtain an appreciation of the properties of the newer steels, it is necessary to describe briefly the changes which have taken place in steel manufacturing technology.

The development of the LD convertor process in Austria in 1948, the first of the top blown basic oxygen furnace (BOF) processes, led to further innovations in the Federal Republic of Germany and subsequently in Japan[16,17] of a whole range of variants of the BOF process.[16–19] These all have special attributes, in particular, reduction of sulphur and phosphorus levels, but not all are equally efficient in this respect and they also vary in process efficiency (i.e. oxygen and ferralloy consumption, yield, etc.). To reduce the load on the BOF,

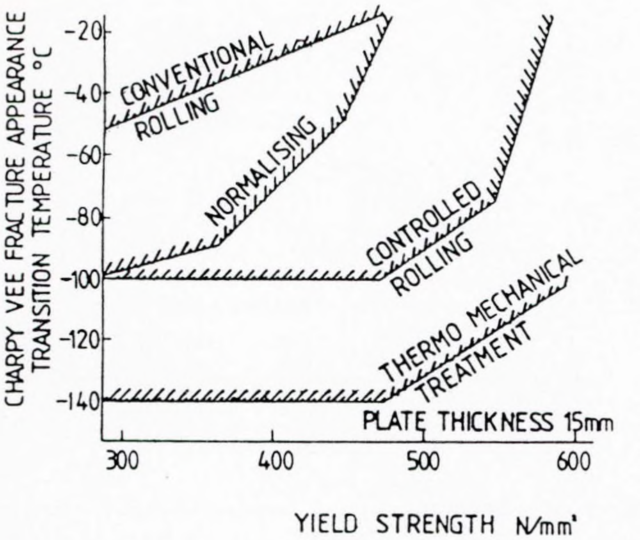



**FIG. 5: Comparison of yield strength properties of conventional and modern steel manufacturing processes[18]**

methods of pretreatment of the hot metal between the blast furnace and the BOF have been introduced to reduce sulphur, phosphorus and silicon levels. Subsequent to tapping the BOF, various secondary refining processes may be applied to the molten steel in the ladle (sometimes called 'secondary steelmaking'). These include vacuum degassing and ladle refining. The former can be used to reduce hydrogen content by up to 70%, to deoxidize, remove oxide inclusions and, in some instances where very low carbon levels are required, to decarburize. Additions of calcium, titanium, zirconium or rare earths may be made immediately before casting in order to achieve sulphide shape control; calcium also has the capability to desulphurize.

A further development which has improved productivity in billet and slab production is continuous casting. In Japan in the 1970–1981 period, continuous casting increased from about 6% to over 70% of constructional steels. The standard techniques for producing plate with good low temperature toughness are normalizing (N), quenching and tempering (QT) and controlled rolling (CR). The most recent developments are essentially two-stage controlled rolling techniques and are described as thermomechanical treatments. The intention of all controlled rolling processes is to achieve fine ferrite grain size to improve mechanical properties and enhance toughness and weldability. Conventional controlled rolling may not achieve optimum grain size and toughness partly because of mixed prior austenite grain size, a feature which is most evident in steels containing niobium and vanadium. Non-uniform structure through the plate thickness may also be related to temperature differences through the thickness during slab heating and rolling. In two-stage controlled rolling, lower slab heating temperatures are used to minimize austenite grain growth. Initial rough rolling is in the range 1100–950°C and the first controlled rolling stage between 920 and 850°C.

The second controlled rolling stage is at lower temperatures finishing below the $Ar_3$ ($\gamma \rightarrow \alpha$) transformation temperature (700–730°C). These thermomechanical treatment procedures treat heating, rolling and cooling as a continuum rather than as discrete processes. A variety of procedures which differ in detail have been developed, principally by Japanese steelmakers, but all achieve broadly similar results. A disadvantage of low finish rolling temperatures is that more powerful rolling mills are required and in some instances roll closing forces of up to 6000 tonnes may be necessary.

A further variant which has been introduced is accelerated cooling on completion of rolling. In this process, controlled rolling is completed above or at $Ar_3$ and accelerated water cooling is applied at a rate between 3 and 12°C/second depending on the grade of steel and plate thickness. The stop or finishing temperature for water cooling is about 550°C and subsequently air cooling is employed. The cooling rate is selected to transform the austenite to fine bainite without any martensite. The stop temperature determines the volume fraction of bainite and affects the hardness of the bainite by an autotempering mechanism. Fracture toughness deteriorates with stop temperatures below about 450°C.

These changes in the manufacturing technology of steels in the past 35 years, many of which have occurred in the past decade, have made possible steel plate materials with greatly improved mechanical and other properties (Fig. 5). A particular problem which has been overcome is low through thickness toughness and ductility in plates and flat rolled products, which result in lamellar tearing in highly restrained Tee-butt and corner welded joints and longitudinal cracking during bending. This has been achieved by elimination of harmful coplanar ribbons of manganese sulphide which may result from low finishing temperatures.

Figure 6 shows the effect of reduction of sulphur level and calcium treatment on through thickness ductility of plate material by reducing sulphur levels, additions of Ca, Zr, Ti or rare earths which convert MnS into less plastic sulphides and also effect inclusion shape control.[15] Such additions may also produce further desulphurization and elements such as Ti may act to produce grain refinement and precipitation strengthening. These latter two features are the essential objectives of microalloying with Nb, V and Ti which act by formation of carbides or nitrides. The various controlled rolling and other procedures are designed to suit the stability of the microalloy carbides and nitrides.

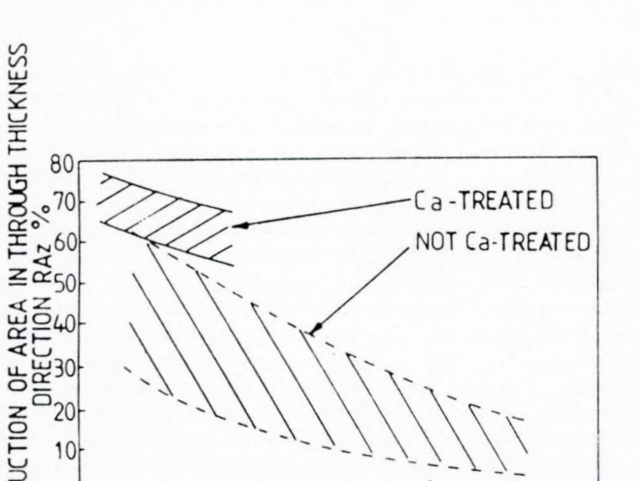



**FIG. 6: Effect of sulphur content and calcium treatment on through thickness properties[14]**

Conventional normalized steels have uniform microstructure and stable mechanical properties but owing to a relatively high carbon content, which is necessary to meet mechanical property levels, they have comparatively high carbon equivalent or CE values, typically 0.34–0.44%. CE is defined as:

$$CE = C + \frac{Mn}{6} + \frac{Cr + Mo + V}{5} + \frac{Cu + Ni}{15}$$

where the chemical compositions are in weight per cent. Higher CE values represent higher hardenability and hence a relatively high preheat temperature is required when welding to prevent cold cracking. The heat input employed in welding is limited to 4–5 kJ/mm to obtain good heat affected zone (HAZ) toughness and to reduce HAZ hardness to avoid danger of environmental stress corrosion cracking. Customers may often specify maximum HAZ hardness levels of 260 to 350 HV for C–Mn steels to be used in offshore structures and this may be difficult for the fabricator to meet in practice.

It has been pointed out[20] that the CE value calculated as above cannot be used reliably as a means for predicting HAZ hardenability, since the formula was originally derived for C–Mn steels in the 1960s when the steels were 'balanced' and not silicon killed. Silicon is not taken into account in the formula nor are the effects of increased cleanliness or the presence of Nb, Ti and Al in enhancing hardenability. Other more complex formulae have been proposed but are not in general use.

Modern steelmaking techniques combined with thermomechanical treatment allow lower CE values (by reduction of carbon and other hardening elements), more isotropic and uniform properties (Fig. 7) and improved toughness without loss of strength. Thermomechanical treatment followed by accelerated cooling can permit even lower CE values without loss of mechanical properties. These modern steels with lower CE values (0.30/0.38%) can be welded with higher heat inputs and in many instances preheating can be dispensed with for thicknesses up to at least 40 mm without risk of cracking (Fig. 8). For heavier material of 50–100 mm thickness, moderate preheating may be necessary in fabrication of restrained features such as node structures. The steels with very low CE values such as are now available (0.27/0.29%) may suffer softening in the HAZ if welded with high heat inputs. Their application is also limited by the fact that, in general, post-weld heat treatment (PWHT) is not acceptable with these low CE materials. Table II shows the chemical composition and mechanical properties of some typical BS 4360 Grade 50D steels produced by thermomechanical working processes in comparison with a normalized grade.

These thermomechanically treated steels have been approved by some of the major classification societies for ship construction and limited quantities have actually been used for bulk carriers, tankers, ore carriers etc. Lloyd's Register has approved such steels for Grades E, AH, DH and EH ship plates and for plates in LT60 Grade for low temperature service. They have also been employed for semisubmersible drilling rigs and at least one jack-up rig, as well as jacket and node steel pipes for platforms.

The requirement to construct offshore structures to operate in deeper waters and also in the more northerly Arctic areas has necessitated development of stronger steels in thicker sections. Exploitation of energy in the Arctic areas[21] involves not only minimum service temperatures of −50 to −60°C but also the effects of ice loading and abrasion, in addition to the normal wind and wave loading. Maximum plate thicknesses of 200 mm may be required in production structures and, for ships such as ice breakers, 75 mm plate with 590 N/mm$^2$ yield stress may be necessary in the bow. For certain applications, 100–200 mm thick material with yield strength as high as 690–900 N/mm$^2$ may be required. Strengths up to around 450–500 N/mm$^2$ can be achieved by alloying with modest levels of Mn, Cu, Ni, Nb and V combined with normalizing; or up to 550 N/mm$^2$ by use of thermomechanical treatment.

For higher strengths, quenched and tempered steels with Ni–Cr–Mo, Ni–Cr–Cu–Mo–B, Cr–Mo–Zr or other combinations of elements such as Cr–Mo, Ni–Mo etc. can be employed. Such materials may have CE values as high as 0.55–0.65%, requiring preheat to 125–150°C when welding, but will have excellent toughness and low temperature properties down to −70° to −80°C in thicknesses up to in excess of 150 mm. These materials compare with the well established HY series of steels HY80 (550 N/mm$^2$), HY100 (690 N/mm$^2$) and HY130 (900 N/mm$^2$) used for naval applications.

Steels for pipeline service, particularly under sour gas conditions (the presence of hydrogen sulphide and possibly also $CO_2$ under wet conditions), require resistance to stress corrosion cracking (SCC) and hydrogen induced cracking (HIC). SCC occurs normal to the surface, whereas HIC is normally

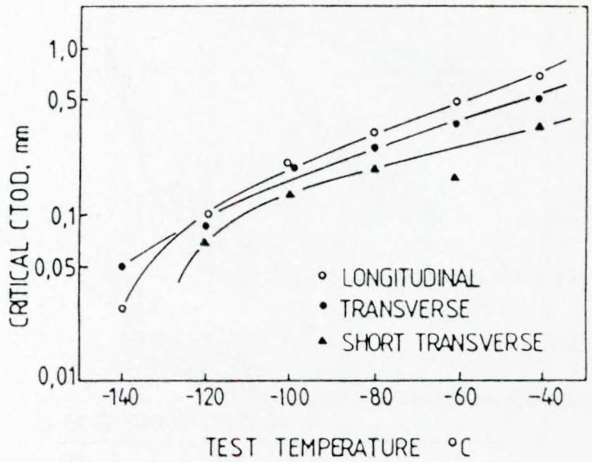



**FIG. 7: Comparative isotropy of thermomechanically treated steel[16]**

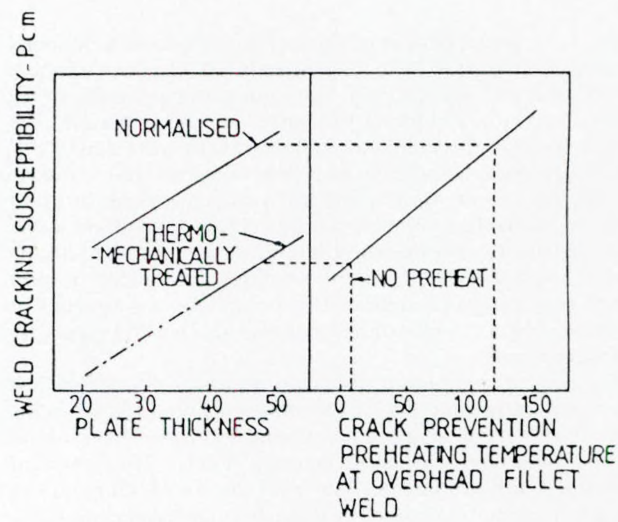



**FIG. 8: Preheating conditions for normalized and thermomechanically treated EH36 plate materials[19]**

internal and parallel to the surface or it may take a step-like path.[17] For protection against SCC, a maximum hardness value of HV 248 has been recommended for steels for sour gas service. Generally, steels which are to resist SCC and HIC are vacuum degassed, low in sulphur (<0.002%), calcium treated for inclusion shape control, have low phosphorus content and restricted levels of manganese. HIC cracks sometimes occur in extremely low sulphur pearlitic steels associated with a microstructural feature known as 'anomalous structure'. This is believed to be a low temperature transformation product of high hardness >450 HV (bainite or martensite), and not ferrite–pearlite. The interface between the normal and anomalous structures is thought to be a plane of weakness. The use of thermomechanically treated steels with or without accelerated cooling enables even heavy wall X65 and X70 grade steel pipe material with excellent low temperature toughness to be achieved by microalloying.

The microalloyed, ultra-clean steels may show, in plates finished rolled below $Ar_3$, a phenomenon known as separation.[16] Intercritical rolling produces a very banded type of microstructure and tensile tests can show separations somewhat similar to those found in laminated plates. The effect

**Table II: Typical thermomechanically treated and normalized steels and properties[19]**

**Composition**

| Steel | Thickness (mm) | Chemical composition % C | Si | Mn | P | S | Ni | Nb | Al sol. | Ti | Cu | N | CE (%) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| A | 50 | 0.12 | 0.26 | 1.36 | 0.016 | 0.004 | — | 0.028 | 0.045 | 0.016 | — | 0.006 | 0.35 |
| B | 50 | 0.07 | 0.16 | 1.39 | 0.018 | 0.002 | 0.29 | 0.026 | 0.028 | 0.017 | — | 0.0071 | 0.32 |
| C | 50 | 0.13 | 0.32 | 1.44 | 0.019 | 0.003 | 0.22 | 0.03 | NA | NA | 0.28 | NA | 0.40 |

A Thermomechanically treated
B Thermomechanically treated + accelerated water cooling
C Normalized

**Mechanical properties**

| | | Tensile properties | | | | Charpy Vee impact | | |
|---|---|---|---|---|---|---|---|---|
| Steel | Direction | YP ($N/mm^2$) | TS ($N/mm^2$) | El (%) | RA (%) | −40°C (J) | −60°C (J) | FATT |
| A | L | 377 | 504 | 34 | — | 214 | | −88 |
| | T | 397 | 515 | 32 | — | 132 | | −72 |
| | Z | — | 511 | — | 75 | | | |
| B | L | 386 | 547 | 30 | — | 267 | 182 | −79 |
| | T | 415 | 534 | 28 | — | 191 | 163 | −77 |
| | Z | — | 527 | — | 64 | — | | |
| C | T | 393 | 525 | | | — | 147 | −55 |

**Weld properties**

| | | | | | Charpy Vee impact | | |
|---|---|---|---|---|---|---|---|
| Steel | Thickness (mm) | Welding process | Heat input (kJ/mm) | Notch position | −60°C (J) | −40°C (J) | −20°C (J) |
| A | 50 | SAW | 5 | Weld | — | 96 | 134 |
| | | | | Fusion zone | — | 139 | 231 |
| | | | 6 | Weld | — | 178 | — |
| | | | | Fusion zone | — | 149 | — |
| | | | 8 | Weld | — | 31 | 57 |
| | | | | Fusion zone | — | 88 | 116 |
| | | | | HAZ | — | 226 | 265 |
| B | 50 | SAW | 3 | Weld | 50 | 97 | — |
| | | | | Fusion zone | 79 | 138 | — |
| | | | | HAZ | 237 | 273 | — |
| | | | 4.5 | Weld | 60 | 70 | — |
| | | | | Fusion zone | 90 | 105 | — |
| | | | | HAZ | 265 | 282 | — |
| | | | 6 | Weld | 44 | 66 | — |
| | | | | Fusion zone | 104 | 127 | — |
| | | | | HAZ | 256 | 294 | — |
| C | 50 | | 3.2 | Fusion zone | — | 49 | — |

becomes evident in tensile tests after maximum load when necking has commenced. The effect is not associated with non-metallic inclusions and is thought to be due to slip between ferrite and pearlite bands and does not represent a potential failure mechanism for materials in service.

A further feature of the modern steels employed in offshore structures is that in some instances certain local regions of the HAZs of welds may show low fracture toughness as characterized by crack tip opening displacement (CTOD) value.[22] The welds and parent material may show high resistance to fracture initiation. The significance of such local regions of low toughness in overall structural integrity is not established nor are the plate compositions, welding procedures, PWHTs etc. which might be selected to avoid the effect under typical fabrication conditions.

## Innovations in welding and joining

It is essential to select the welding or joining processes which are to be used in fabrication to suit the material. In many instances the modern steels have been developed with improved weldability as an objective; in particular, suitability for higher heat input and automated processes with reduced need for preheat and, if possible, enhanced as-welded properties.

The move to automatic and also less operator-sensitive processes is well illustrated by experience in the construction of submarines for the Royal Navy in QT HY80 type material. At present about 87% of welds are manual metal arc (MMA), 3% MIG and 10% submerged arc in terms of weight of consumables.[23] The Ministry of Defence has sponsored the development by The Welding Institute of automated pulsed metal inert gas (MIG) equipment which is currently under evaluation in the shipyard.[24] This process is expected to replace MMA for a wide range of welding tasks and will enable the welder to concentrate on positioning of the weld, since optimum weld parameters can be maintained automatically. It is estimated that there will be a saving of up to 40% in consumables. There is also interest in narrow gap processes possibly using pulsed MIG.

Other narrow gap processes have been under investigation since the late 1960s, including electron beam (EB) and laser beam (LB) welding.

EB welding produces a deep, narrow weld, usually in a single pass with fine grain size and small HAZ. The low heat input and resulting low distortion, combined with the high rate of joint production, make EB welding attractive for joining thick sections. Complexity, the need for accurate edge register, high capital cost and the current need to weld in vacuum are obstacles to the use of the process for large structures. However, developments in out-of-vacuum EB welding may overcome some of these problems, although the hazard of X-ray generation could be an obstacle to industrial use of the process except under carefully controlled conditions. Nevertheless, conventional EB welding is being actively assessed for welding of subassemblies for submersibles and in France[25] a full scale apparatus has been developed for single pass EB welding of pipelines up to 610 mm OD by 32 mm wall thickness. The intention is to employ a dynamically positioned vessel using the J-curve pipe laying technique.

The MOD took the lead in the development of LB welding in the UK in conjunction with The Welding Institute and other organizations. In the UK, currently available continuous $CO_2$ lasers with power levels up to about 10 kW are able to weld up to 12–15 mm in low alloy steels such as HY80, HY100 and HY130; also in the microalloyed structural steels. Owing to the high cooling rates in EB and LB welds, the fusion zone and HAZ hardnesses in the low alloy steels may exceed HV 400 and corrosion fatigue crack growth rates in seawater may be unacceptable without PWHT. In addition, certain batches of material may show poor weld metal centreline toughness but there are indications that, by control of residuals and PWHT, this problem can be overcome. The use of a nickel alloy shim in

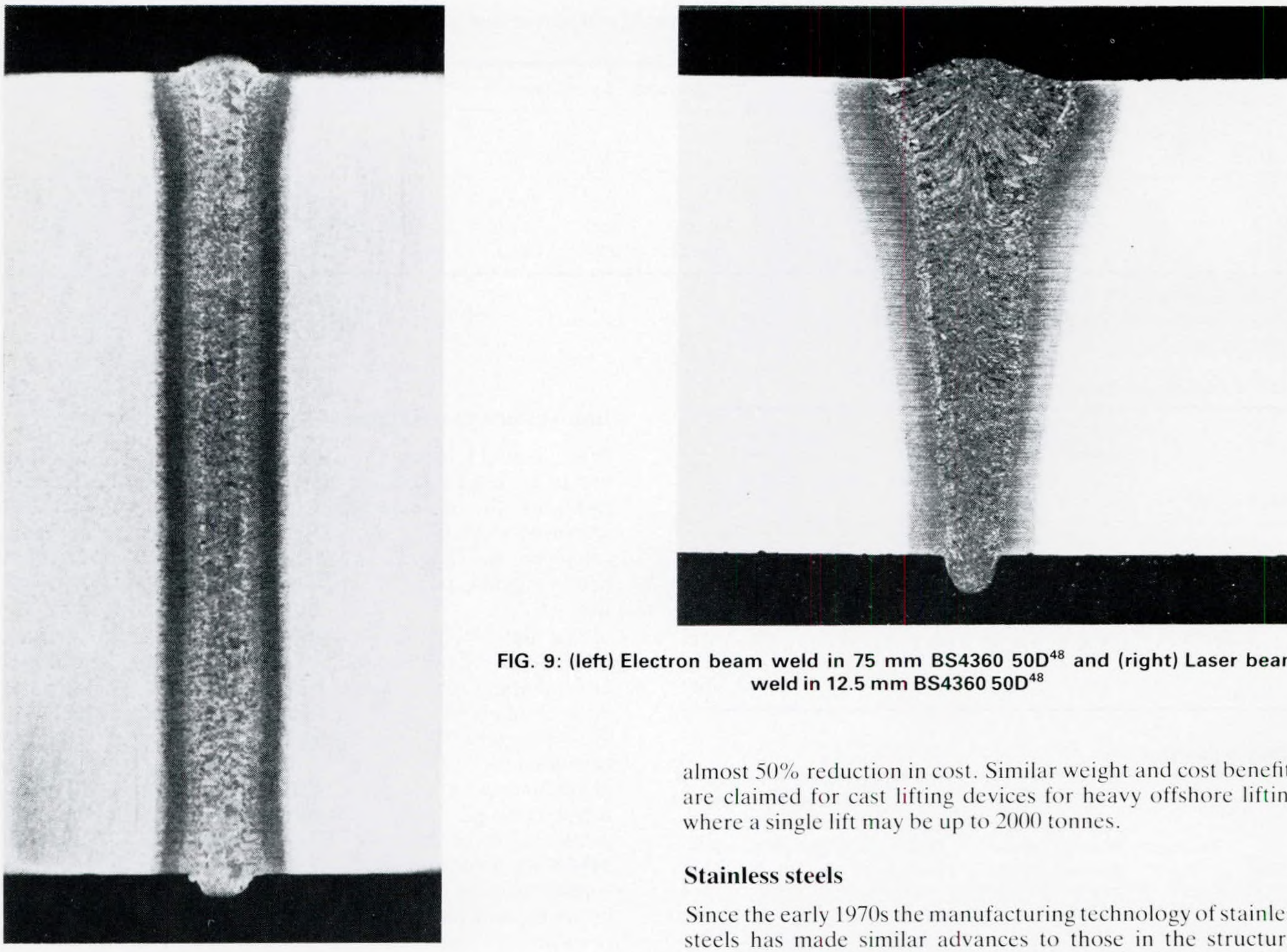


**FIG. 9: (left) Electron beam weld in 75 mm BS4360 50D[48] and (right) Laser beam weld in 12.5 mm BS4360 50D[48]**

the weld preparation has also been found to improve the weld metal properties in LB welds. Electron beam and laser welds are shown in Fig. 9.

In the 1970s considerable development took place in underwater welding and research is still in progress, particularly in relation to wet welding as distinct from dry habitat or minihabitat welding. Objectives tend to be improvement of electrodes and welding procedures to enable welding in deeper water of more than 100 m in a wider range of situations and materials.

Recent developments in friction welding which appear to have potential in the offshore industry are radial friction welding for pipelines[26] and underwater friction welding of attachment studs to platform structures.[27]

## Steel castings

Whilst cast HY80 or its UK equivalent Q1N has been employed for many years in submarines for complex cast components such as hull valves and other steels in ships for stern frames, it is only recently that major cast structural components have been used in offshore structures.

In the past 7 years in the UK[28] and FRG[29], cast steel node components and padear and other castings for lifting points have been developed. The UK steel was designed to be compatible with BS 4360 Grade 50D in terms of mechanical properties and weldability and is essentially a fine grained, pearlite reduced microalloyed steel containing small amounts of molybdenum (see Table III). Cast nodes show a significant reduction in stress concentration factor (SCF) and hence improved fatigue performance compared with comparable fabricated nodes. In one particular example, a 108 tonnes weld fabricated node was reduced to a 70 tonnes casting with an almost 50% reduction in cost. Similar weight and cost benefits are claimed for cast lifting devices for heavy offshore lifting where a single lift may be up to 2000 tonnes.

## Stainless steels

Since the early 1970s the manufacturing technology of stainless steels has made similar advances to those in the structural steels: in particular, the argon–oxygen decarburization (AOD) process and the use of vacuum induction and vacuum arc melting.[30] The AOD process and its variants permitted control of carbon without excessive loss of chromium. Carbon could be reduced to much lower levels, the major alloying elements could be controlled more precisely, nitrogen could be a controllable alloying element and impurity elements (e.g. S, Pb, Sn, Bi) detrimental to hot working could be reduced significantly. These developments have permitted evolution of compositions of austenitic, ferritic and duplex (austenitic/ferritic) stainless steels with higher alloy content and improved resistance to pitting, crevice corrosion and stress corrosion under marine conditions.

Some examples of modern stainless steels are shown in Table IV. The principal factor contributing to the improved performance of stainless steels in seawater and marine conditions generally has been increased molybdenum content, which has provided enhanced pitting and crevice resistance. The level of molybdenum is fairly critical and, of the austenitic steels, whilst steel No. 1 is much better than, say, 316 (2–3% Mo), it is still susceptible to crevice attack in artificial crevices and under biofouling. Steel No. 2 with high Mo is more resistant and in excess of $8 \times 10^6$ m of tubing is in service in seawater cooled condensers in North America. There is some similar experience in Europe with steel No. 3. This type of steel has also been used[31] for the high pressure pipe systems of seawater reverse osmosis plant for fresh water production. It is known to perform well in the brine outlet side with 30000 ppm chlorides. The resistance to stress corrosion of these higher alloyed austenitics is also believed to be better under chloride conditions but each use needs to be assessed carefully. Standard laboratory testing procedures using boiling, 42% $MgCl_2$ may be unduly severe and unrepresentative of actual plant conditions and materials failing this test may perform quite adequately in service.

**Table III: Composition and properties of cast node steel[28]**

| Typical chemical composition (%) | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| C | Mn | Si | P | S | Nb | V | Mo | Ni | Cu | Ti | Al | CE (%) |
| 0.13 | 1.29 | 0.30 | 0.010 | 0.002 | 0.023 | 0.04 | 0.12 | 0.41 | 0.05 | 0.01 | Present | 0.43 |

| | Mechanical properties | | | | | |
|---|---|---|---|---|---|---|
| | *YS* ($N/mm^2$) | *TS* ($N/mm^2$) | *El.* (%) | *R of A* (%) | *Charpy at* −40°C (J) | *CTOD at* −10°C (mm) |
| Specification min. values | 320 | 460 | 20 | 45 | 35 | 0.25 |
| Typical | 340/360 | 480/510 | 30 | 70 | 70/100 | 0.8/1.2 |

In the ferritic grades, control of interstitial elements such as carbon and nitrogen has enabled greater alloying with chromium and molybdenum without impairing toughness and weldability. Steel No. 6 in Table IV has inadequate crevice resistance for use in seawater but if the Mo content is increased to above 3% resistance is greatly enhanced. Steel No. 7 has been used successfully in seawater condensers and more than $2.4 \times 10^6$ m of condenser tubing are already in service. Tubing can be made by welding and is claimed to have advantages over 90/10 CuNiFe and titanium. The ferritic stainless steels also show much better resistance to stress corrosion than the austenitics in chloride environments. Control of composition has enabled materials of up to 12 mm thick to be manufactured with adequate toughness but the problem of thicker plate with appropriate toughness and weldability still remains to be solved.

The duplex stainless steels have the advantage of greater strength than the austenitics (double the proof stress and 25% greater tensile strength) and are tougher than the ferrites but can match their resistance to pitting, crevice and stress corrosion. Although not immune to chloride stress corrosion under all circumstances, the duplex materials do have good corrosion fatigue properties. Steels such as No. 11 have been used for pipes carrying wet $CO_2$-containing gas and can eliminate dehydration equipment on satellite platforms. It has also been used for air-cooled gas coolers, down-hole piping, deep sour gas well production tubulars, flowlines and gathering systems and there has been some limited use for riser pipes, particularly to resist splash zone corrosion effects. Alloys 12 and 13 have found application in oilfield water injection pumps,[31] and small cast marine propellers.

## NON-FERROUS MATERIALS

### Copper alloys

The scale of usage of copper alloys in marine and offshore applications is not surprising in view of the availability, general fabricability and mechanical properties combined with acceptable corrosion resistance, favourable antifouling properties and useful physical properties. Recent developments in copper base alloys have been in improved understanding of design of castings together with running, gating and feeding systems to achieve sound castings, the use of centrifugal casting, introduction of higher strength cast cupronickel alloys and some novel wrought materials. Application of copper alloy cladding has also been exploited and this will be described later in the paper.

The Royal Navy has employed cast nickel aluminium bronze (NAB) in high integrity seawater systems for many years but, due to the complex microstructure of the alloy and its somewhat low resistance to fouling, some corrosion has occurred locally under biofouling or other deposits or in way of weld repairs in the HAZ. A number of high strength cast cupronickel alloys[32] have been evaluated as potential alternatives over the period since the late 1960s. Although some of these existed in reasonably well characterized experimental form when the need for a high strength alloy was first identified, NAB was used since it could be melted in the oil and gas fired furnaces with which most non-ferrous foundries were equipped. Cupronickel alloys, particularly those with 30% nickel which were considered necessary for high corrosion resistance, could only be melted in electric furnaces, at that time unusual in all but high nickel alloy and steel foundries. The position has changed in the past decade and electric furnace capacity is now fairly common since the advantages of electric melting have been more widely appreciated, the faster melting and cleaner furnace atmospheres resulting in a superior quality product. The two Cu–Ni casting alloys which have been evaluated most extensively, including trials of up to several years duration on prototype or 'demonstrator' components such as condenser

**Table IV: Some modern stainless steels[30]**

| | | Nominal chemical composition (%) | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| *No.* | *Type* | Cr | Ni | Mo | C | N | Cu | W | T | Ti + Nb | Nb |
| 1 | Austenitic | 19/23 | 23/28 | 4/5 | 0.02 | — | 1/2 | — | — | — | — |
| 2 | | 20/22 | 23.5/25.5 | 6/7 | 0.03 | — | — | — | — | — | — |
| 3 | | 19.5/20.5 | 17.5/18.5 | 6/6.5 | 0.02 | 0.18/0.22 | 0.5/1.0 | — | — | — | — |
| 4 | | 27 | 31 | 3.5 | — | — | 1.0 | — | — | — | — |
| 5 | | 22/26 | 33/37 | 5/6.7 | 0.03 | — | 2/4 | — | — | — | — |
| 6 | Ferritic | 25/27 | — | 0.7/1.5 | 0.01 | 0.015 | — | — | — | — | 0.05/0.20 |
| 7 | | 25/27 | 1.5/3.5 | 2.5/3.5 | 0.025 | 0.035 | — | — | — | (a) | — |
| 8 | | 24.5/26 | 3.5/4.5 | 3.5/4.5 | 0.025 | 0.035 | — | — | — | (a) | — |
| 9 | | 28/30 | 2/2.5 | 3.5/4.2 | 0.01 | 0.020 | — | — | — | — | — |
| 10 | Duplex (A + F) | 18/19 | 4.25/5.25 | 2.5/3.0 | 0.03 | — | — | — | — | — | — |
| 11 | | 21/23 | 4.5/6.5 | 2.5/3.5 | 0.03 | 0.08/0.20 | — | — | — | — | — |
| 12 | | 24/27 | 4.5/6.5 | 2/4 | 0.04 | 0.1/2.5 | 1.5/2.5 | — | — | — | — |
| 13 | | 24/26 | 5.5/7.5 | 2.5/3.5 | 0.03 | 0.1/0.2 | 0.2/0.8 | 0.1/0.5 | — | — | — |

(a) Ti + Nb = (0.20 + 4(C + N) − 0.80)

(A)

Table V: Composition and properties of two high strength cupronickel casting alloys

| Alloy | Cu | Ni | Fe | Mn | Si | Cr | Zr | Pb max. | P max. | Bi max. | Nb + Ta | S max. | C max. | Co max. | Total imp. max. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | *Specified chemical composition* (%) | | | | | | | | | | | | | | |
| IN 768* BS 1400 HSCN1 | Bal | 29/33 | 0.4/1.0 | 0.4/1.0 | 0.2/0.4 | 1.5/2.0 | 0.05/0.15 | 0.005 | 0.005 | 0.002 | — | 0.01 | 0.03 | 0.05 | 0.2 |
| Cu–Ni–Nb–Si BS 1400 HSCN2 | Bal | 28/32 | 1.0/1.4 | 0.4/1.0 | 0.2/0.4 | — | — | 0.005 | 0.005 | 0.002 | 1.2/1.4 | 0.01 | 0.03 | 0.05 | 0.2 |

(B)

| Alloy | Tensile strength ($N/mm^2$) | 0.2% Proof stress ($N/mm^2$) | Elongation in 50 mm (%) |
|---|---|---|---|
| | *Mechanical properties* | | |
| IN 768* | 480 min. | 300 min. | 18 min. |
| IN 768* | 514 typical | 336 typical | 26 typical |
| Cu–Ni–Nb–Si | 460 min. | 300 min. | 18 min. |

*Proprietary alloy, Inco Alloy Products.

headers and bow thruster components on MCMVs, are shown in Table V together with mechanical properties.

Although BNFMTC have derived casting design and foundry rules for the alloys and sound castings can be produced without difficulty, there may be a requirement for either weld repair or rectification or cast/weld fabrication in future and hence weldability is important. In common with other copper base alloys the cupronickels show a ductility trough in the range 500–600°C, which can give rise to cracking problems in welding. This is believed to be related to impurity levels, grain boundary effects and grain size. Hence certain casts may require care in welding but MMA, MIG and TIG welding techniques have been used successfully.

Centrifugal casting is a process which has only in recent years been applied to high strength copper alloys for marine applications. In the past 5 years the Royal Navy has evaluated NAB header castings fabricated by centricasting in the UK and Europe. The process looks economically and technically attractive in comparison with traditional sand casting.

In recent years a new metallurgical strengthening mechanism known as 'spinodal' decomposition has been recognized and exploited in practical alloys. The first example in marine alloys was IN 768, discussed above. This mechanism can be used to develop a wide range of mechanical and physical properties similar to precipitation hardening. However, spinodal alloys tend to be more ductile at a given strength level than other alloys and more stable during heat treatment than precipitation hardening materials. A number of alloy systems show the phenomenon (the mechanism of which is beyond the scope of this paper), including Cu–Ni–Sn alloys.[33] Materials are treated in a similar way to precipitation hardening materials, i.e. solution treat, water quench (WQ) and age; or solution treat, WQ, cold work and age. Solution treatment for the Cu–Ni–Sn alloys is in the range 700–860°C and ageing is between 300 and 400°C, the precise temperatures depending upon alloy composition. The materials can also be produced in cast form as sand or centrifugal castings. Alloy designations and properties are given in Table VI in comparison with phosphor bronze and beryllium copper.

The alloys are reputed to have good corrosion resistance in seawater, e.g. the Cu–10Ni–8Sn alloy in the solution treated and aged condition is reported to have a corrosion rate of 7.1 $mg/dm^2$/day in seawater. The alloys are also stated to have good fatigue properties, stress relaxation resistance and formability. The C72800 alloy has been used for high strength marine fasteners (1000 $N/mm^2$ tensile strength; 689 $N/mm^2$ 0.01% offset proof stress). Extruded and also sand and centrifugally cast parts in this alloy have been used for undersea cable repeater housings. The C72900 alloy has been used for corrosion/erosion resistant weld overlays deposited by TIG welding on silicon bronze pump impellers for seawater service and its use for cast pump bodies has been proposed, as has C96800 for similar duty.

## Titanium

Titanium and its alloys have now been under development for about 30 years and usage in seawater applications in the UK and North Sea totals about 3000 tonnes.[34,35] In view of this limited use of titanium in marine and offshore applications it still qualifies as a relatively new material, in the sense that it is applied less widely than its properties indicate that it could be with technical and economic advantage. It is strong, light (density 4.50 $kg/m^3$), has a modulus of elasticity about half that of steel and is non-magnetic. It has excellent corrosion resistance in seawater under static or flowing conditions and can tolerate very much higher flow velocities in pipe systems than the established copper base alloys such as 90/10 CuNiFe and 70/30 CuNiFe.

The high strength titanium alloys do not stress corrode in the conventional sense since they require an initiating feature such as a surface precrack, although they do appear to suffer crack propagation when precracked specimens are loaded in seawater. The phenomenon has sometimes been referred to as sustained load cracking. However, the use of material with extra low interstitial levels (ELI) (i.e. carbon, oxygen, hydrogen and nitrogen) can render sustained load cracking less sensitive to processing and heat treatment variations.

Table VI: Mechanical properties of copper–nickel–tin alloys in strip form[33]

| Alloy designation | Type | Condition | TS ($N/mm^2$) | Proof stress ($N/mm^2$) | Elongation (%) |
|---|---|---|---|---|---|
| C72600 | Cu–4Ni–4Sn | ¼H + A | 620 min. | 517 (0.05%) | 12 |
| | | ST + A | 703 min. | 586 (0.05%) | 7 |
| C72700 | Cu–9Ni–6Sn | 78%CW + A | 1103 | 931 (0.05%) | 2.5 |
| C72800* | Cu–10Ni–8Sn + Nb | ¼H + A | 1172 min. | 1000 (0.2%) | 7 |
| C72900 | Cu–15Ni–8Sn | 78%CW + A | 1124 min.<br>1379 max. | 1069 (0.05%)<br>1172 (0.05%) | 2 |
| C51000 | Phosphor bronze | CW | 738 | 552 (0.5%) | 3 |
| C17200 | Cu–Be | ST + A | 1310 min.<br>1517 max. | 1138 (0.2%) | 1 |

*C96800 for castings

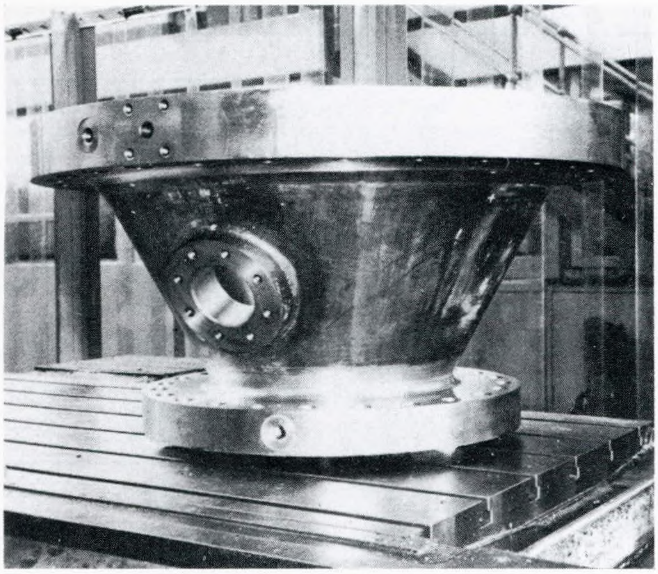


FIG. 10: Fabricated titanium header

In practice, alloys such as Ti–6Al–4V have been used quite successfully in a wide range of applications as also has commercially pure (CP) titanium. Titanium is not intrinsically antifouling and hence marine fouling can occur but no crevice or other enhancement of corrosion is found beneath deposits. It is also resistant to sulphide polluted seawater. The resistance of titanium to hypochlorite enables chlorination or hypochlorite to be used to prevent biofouling.

Marine engineering systems (e.g. seawater systems) generally involve dissimilar metals and since titanium is more noble than most established marine materials it is cathodic in most bimetallic couples and the corrosion of the anodic member(s) may be accelerated. The rate of corrosion of a particular metal[36] will depend on the current flowing between the dissimilar metals in relation to their surface areas. This depends upon the polarization characteristics of the metals, the resistance of the metallic and electrolytic paths and respective areas of the anode and cathode components and is frequently not related directly to the uncoupled electrode potential difference. Practical systems often have complex geometries and the effective surface area ratio differs from the physical area ratio, owing to the resistive losses in the electrolyte. Recently,[36] mathematical models have been developed so that the magnitude and distribution of corrosion rates in such systems can be calculated using computer techniques. Clearly the most compatible alloy combinations should be selected and a range of techniques can be used to overcome bimetallic corrosion including insulation, coating of the titanium or cathodic protection.

The possibility of hydrogen absorption by titanium with consequent embrittlement due to hydride formation has been discussed and researched a great deal. Essentially it has been suggested that although a surface layer of hydride may form under certain conditions, diffusion into the bulk material is not significant below about 80°C. Short term data are not a reliable indication and only isolated instances have occurred in service. Understanding of the phenomenon is now sufficiently broad to enable avoidance in most applications.

Titanium and titanium alloys are being considered for use in high pressure, high integrity seawater systems in RN submarines,[24] since they offer attractive strength and other properties compared with traditional wrought and cast copper base alloys. Both cast and wrought materials are being assessed and a CP titanium condenser header fabricated from forged components is shown in Fig. 10. Successful applications of titanium in RN warships include tubing in drain coolers where 70/30 CuNiFe suffered 'hot-spot' corrosion, diesel exhaust scrubber systems and hull bolts on mine countermeasures vessels, compressor blading and discs in marine gas turbines, balls in seawater ball valves and a variety of other components where problems were experienced or anticipated with more traditional materials.

Small deep submersibles have been fabricated in the USA and France from titanium alloy and the Ti–6Al–4V alloy has been used in hydrofoil components such as struts, foils and water jet propulsion units.[34,35] Propeller shafts for hovercraft have also been made in titanium alloy. Other applications of titanium include anchor lugs for cathodic protection anodes, hypochlorite water treatment plants and electrolytic hypochlorite generators, for treating water for reinjection into oil wells or for prevention of biofouling in flooded steel structures. The most extensive use of titanium so far in the North Sea has been in heat exchangers for product and glycol cooling.

## NICKEL ALLOYS

Many established nickel base alloys developed for general engineering and process plant applications have been found to have special attributes in the marine environment and in seawater and have been applied increasingly in recent years in marine applications. Other alloys have been developed specifically to overcome problems encountered, for example, in marine gas turbines at elevated temperatures.

A widespread use of high nickel alloys developed in the 1970s for scrubber systems in inert gas systems in oil tankers.[37] Boiler exhaust gas is scrubbed to remove soot and sulphur oxides and the resulting inert gas is forced into the airspace above the oil cargo, flushing out the volatile (and potentially explosive) hydrocarbons which would normally be present. The inert gas consists of nitrogen with carbon dioxide and about 4% of oxygen. To support combustion of hydrocarbon/air mixtures about 12% or more oxygen is required. Seawater is used for scrubbing. A variety of different inert gas systems are in operation and in some Incoloy 825 (see Table VII) has proved satisfactory while in others use has been made of Inconel 625, a lower iron, higher nickel, higher molybdenum, but stronger and more expensive alloy. These materials have also been used for bellows. The environment in scrubbers contains chlorides in the presence of acid seawater (due to dissolution of sulphur oxides) and pH values can be as low as 1–1.5 with temperatures up to 50°C. The nickel alloys have good pitting resistance in chloride environments and crevice corrosion resistance improves with increasing molybdenum content, Inconel 625 (8–10% Mo) being virtually immune to crevice attack in seawater. Increasing nickel content also improves chloride stress corrosion resistance and alloys with more than about 50% nickel are substantially immune.

A somewhat similar application of high nickel alloys has been proposed in the compressor section of certain marine gas turbines, where pitting of blading due to seasalt in the presence of acid condensate under shutdown conditions led to fatigue failure of precipitation hardened stainless steels. The acid condensate arises from ingestion of funnel gas containing sulphur oxides from oil burning boilers in the ship or from other ships alongside in port. A change to titanium blading was one effective solution but would have entailed redesign of the compressor discs. A more simple solution was to change to IN 718, which was shown in laboratory investigations to be much more resistant to pitting by seasalt/acid condensate and to have much enhanced 'corrosion induced' fatigue resistance (the phenomenon was not considered as standard corrosion fatigue). IN 718 also appears to have potential as a high strength corrosion resistant spring material in marine environments.

Ingestion of seasalt and sulphur from fuel can lead to aggressive environments in gas turbines operating in marine conditions, resulting in corrosion damage to hot-end components, even in well filtered engines.[38] Distillate fuels such as

**Table VII: Some nickel base alloys with new marine applications**

| Alloy | Alloy chemical composition (%) | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | C | Mn | Fe | Cu | Ni | Cr | Al | Ti | Mo | Nb + Ta | Co | Si | S | Other |
| Incoloy 825 | 0.03 | 0.5 | 30.0 | 2.2 | 42.0 | 21.5 | 0.1 | 0.9 | 3.0 | — | — | 0.2 | 0.02 | — |
| Inconel 625 | 0.05 | 0.2 | 2.5 | — | Bal | 21.5 | 0.2 | 0.2 | 9.0 | 3.6 | — | 0.2 | 0.008 | — |
| 901 | 0.05 | 0.08 | Bal | 0.05 | 41.7 | 12.55 | 0.24 | 2.96 | 5.76 | — | 0.12 | 0.21 | 0.004 | B 0.014 |
| IN 718 | 0.47 | 0.10 | 18.5 | 0.25 | Bal | 18.5 | 0.57 | 1.2 | 3.1 | 5.0 | 0.03 | 0.24 | 0.004 | B 0.0054 |
| INCO 738 | 0.17 | 0.2 | 0.5 | — | Bal | 16.0 | 3.5 | 3.4 | 1.7 | Nb 0.9 | 8.5 | 0.5 | B 0.01<br>Zr 0.10 | W 2.6<br>Ta 1.7 |
| IN 939 | 0.15 | — | — | — | Bal | 22.5 | 1.9 | 3.7 | — | Nb 1.0<br>Ta 1.4 | 19.0 | — | — | W 2.0<br>Hf 1.0<br>Zr 0.1<br>B 0.01 |
| IN 6201* | 0.025 | — | — | — | Bal | 20.0 | 2.5 | 3.6 | 0.5 | Nb 1.0<br>Ta 1.5 | 20.0 | — | — | W 2.3<br>Zr 0.05<br>B 0.8 |

*UK Patent 1544720.

gas oil normally contain about 1% of sulphur and sulphur oxides in the combustion gases in conjunction with seasalt can lead to hot corrosion damage at temperatures above about 650°C. Paradoxically, the most severe damage may occur at around 700°C with most superalloys and protective coatings. The phenomenon is, in general, similar to boiler fireside corrosion and was first identified in early generation gas turbines in Royal Navy warships in the 1960s and was associated with turbine first-stage blade temperatures in the range 650–750°C (see Fig. 11). Propulsion engines in warships may spend a high proportion of life at low temperatures with only 5% of life at full power and the major operating time at part-load conditions. Hence, even engines designed with first-stage turbine blade temperatures in the 850–950°C range may operate mainly in the region around 700–750°C. In addition, many engine types are designed with first-stage blade cooling, which inevitably results in some area adjacent to the blade root or platform operating in this temperature range. In cooled blades this low temperature region extends further up the mid-chord of the blade as power is reduced. The phenomenon is not peculiar to propulsion engines in ships but is also found in engines on offshore platforms when operating on commercial gas oil, as distinct from low sulphur gas which may be the case when gas is not flared.

The high strength nickel base superalloys employed in aero gas turbines tend to have relatively low chromium content and special higher chromium alloys have been developed (such as IN 738, IN 939 and IN 6201, see Table VII) in recent years to combat hot corrosion in marine gas turbines. The Royal Navy has played a prominent role in encouraging and/or sponsoring these developments. Equally, pack aluminized coatings are unsatisfactory for resisting hot corrosion on first-stage blading in marine gas turbines and the Royal Navy has carried out a large research and development programme to identify improved coating materials and application techniques, as described later. The compositions of some of the newer alloys are shown in Table VII and their corrosion properties in comparison with established nickel base superalloys are shown in Fig. 12, the data being derived from extensive combustion rig tests.

In the offshore industry, 825 and 625 alloys have been employed in plate heat exchangers and expansion bellows in decklines and steamlines. There has also been interest in high nickel alloys for deep sour gas well production tubulars. Use has been made of 825 in gas compressor intermediate coolers where $H_2S$, $CO_2$ and salt water are encountered in the product and resistance to stress corrosion is required.[11] Corrosion of carbon steel hot oil riser pipes in the splash zone (up to 2.5 mm/year) has been encountered in the North Sea and elsewhere and 625 has been employed as a satisfactory alternative.

**FIG. 11: Corroded gas turbine rotor blade**

## CLAD MATERIALS AND METALLIC COATINGS

Clad materials and coated materials with coatings applied by thermal spray, plasma and other more advanced techniques potentially combine the attributes, economic and/or technical, of two or more materials in a single product. Traditionally, the role of metallic coatings and claddings has been to endow low cost materials with a more corrosion resistant surface in order to arrive at a more economic or stronger structure than could be achieved by the use of monolithic, corrosion resistant, high cost materials. In addition, coatings have been employed to provide some special attribute such as hardness, wear resistance, erosion resistance, tribological compatibility, non-slip properties, resistance to high temperature oxidation etc. on critical areas of surfaces. Increasing use has been made of

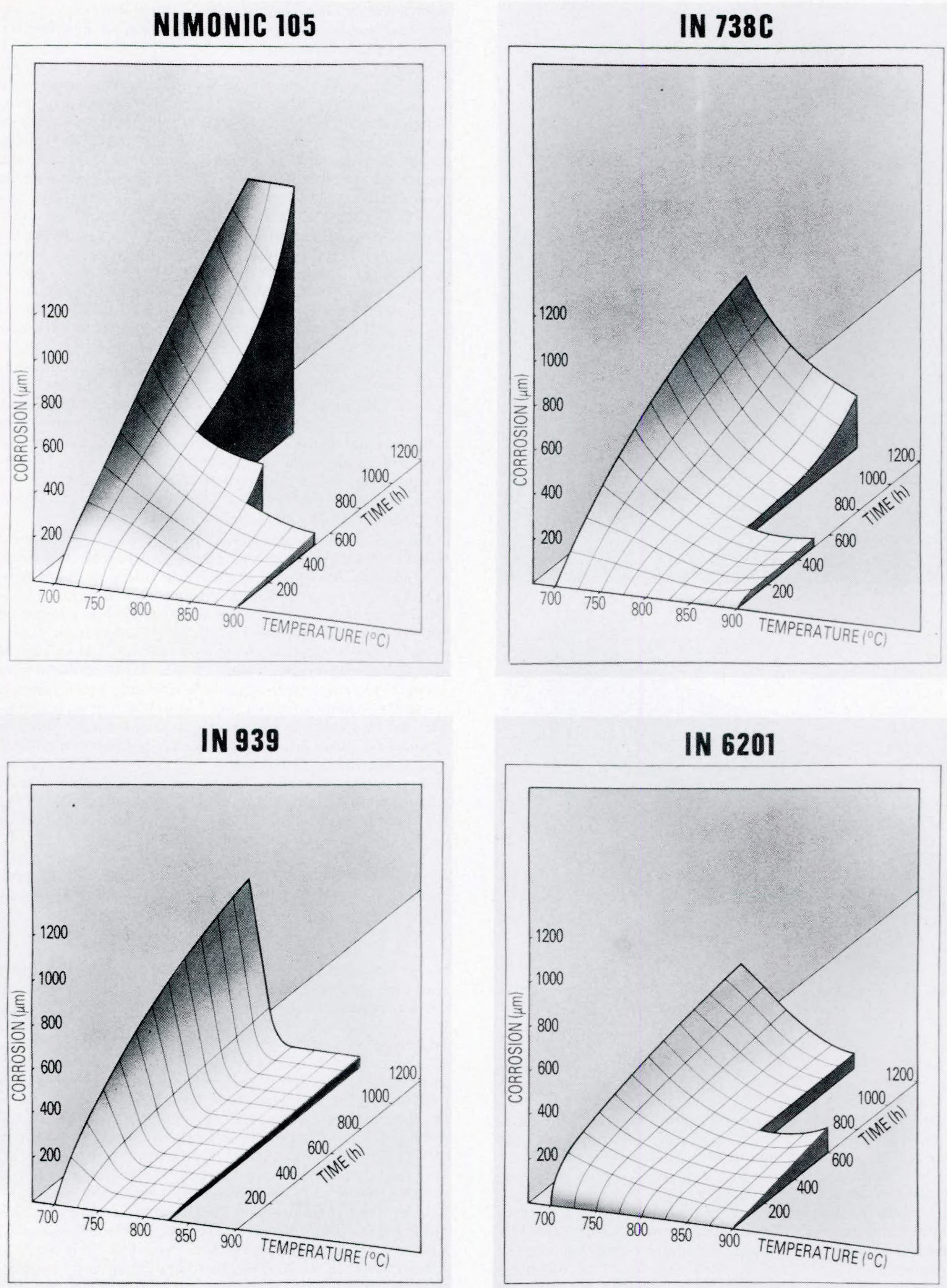



FIG. 12: Hot corrosion properties of some nickel base superalloys

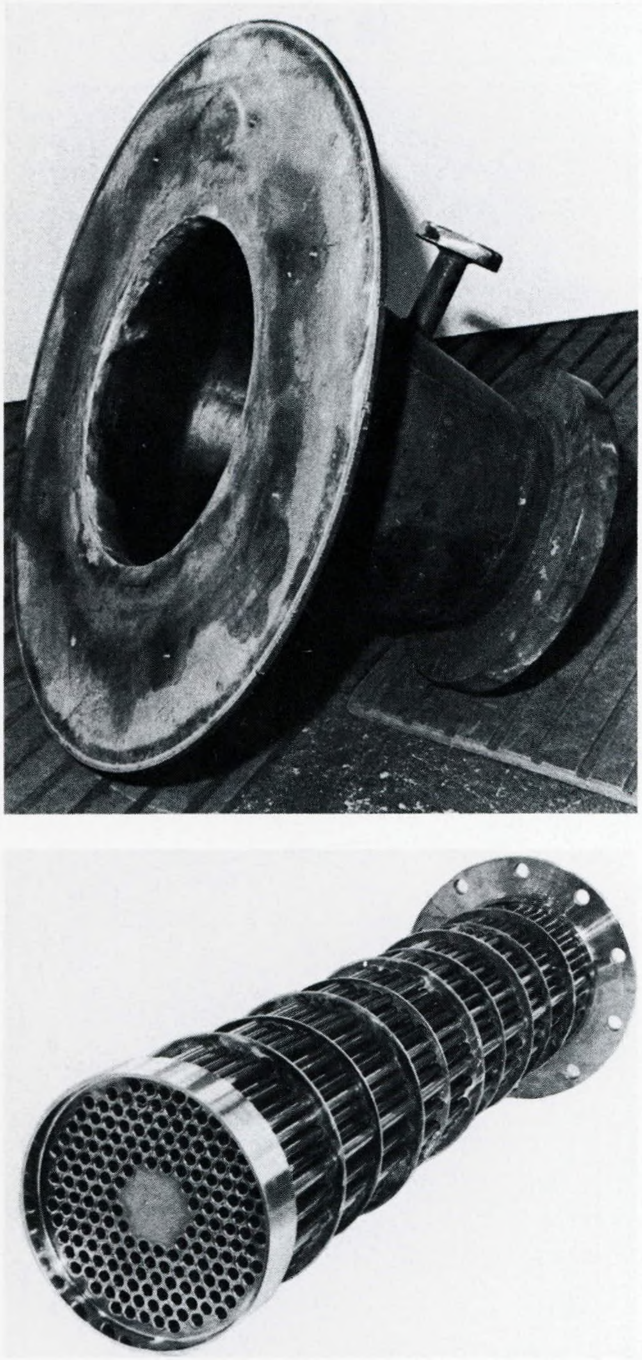


**FIG. 13: 90/10 Cupronickel plug weld clad sea tube and 70/30 fusion weld clad tube plate**

thermal spray coating and weld cladding processes for reclamation and repair of worn or corroded components with savings in cost and/or time. Non-metallic polymeric coatings have been employed to protect components from cavitation damage in fast flowing turbulent liquids.

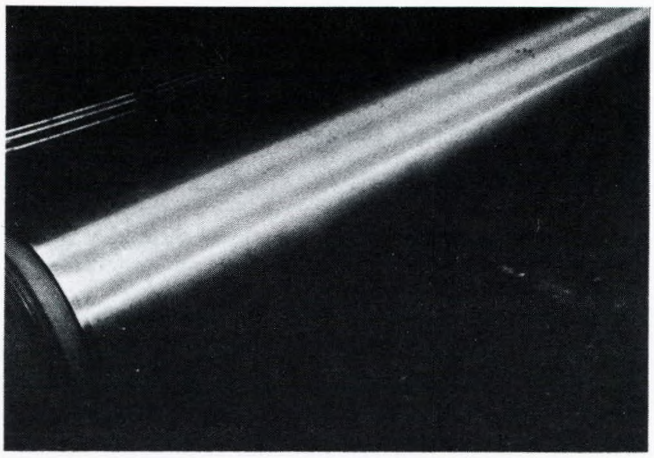
Metallic cladding may be achieved by a wide variety of processes, including fusion welding by manual metal arc, TIG or MIG welding, inert gas plug welding to attach thin layers of corrosion resistant sheet to steel, explosion and roll bond cladding. Diffusion bonding offers a further possibility in special instances. Recent research at The Welding Institute has demonstrated that the high power $CO_2$ laser may be used to deposit cladding metals, using wire as in TIG welding but with much lower dilution from the substrate steel. Friction surfacing has also been shown to be an effective way of applying thin (1 mm) surface layers.

Thermal spray coatings may be deposited by the flame, arc and plasma arc processes and recent developments in the field of high velocity, low pressure, inert gas, plasma spray techniques have led to very high integrity coatings. The use of controlled laser fusion in combination with traditional flame or plasma coatings offers a further possibility of high integrity and specialized coatings. For special applications, electron beam evaporated coatings, high rate sputtering or other more complex PVD processes such as ion plating may be employed. Chemical vapour deposition (CVD) may also be appropriate.

In the past decade, extensive evaluation has been carried out by the Royal Navy of a wide range of cladding techniques applied to trial components, many of which have been used in service with entirely satisfactory results. Sheathing with 90/10 cupronickel sheet employing MIG plug welding and TIG seam welding provides a successful technique for applications where service stresses and fatigue levels are low. For more demanding conditions, metallurgically bonded cladding must be used. Figure 13 shows a plug weld clad sea tube and a fusion clad oil cooler tube plate. Condenser headers have been fabricated from steel clad with cupronickel by fusion weld deposition, roll bond and explosion cladding. In certain foreign navies and also in some merchant ships, explosion bonded steel/aluminium transition pieces have been employed to enable weld attachment of aluminium superstructure to steel decking.

Since 1973, sharp increases in fuel costs have focused attention on reducing the hull roughness of ships to reduce frictional drag and enhance operating efficiency. Every 10 $\mu$m increase in hull roughness is estimated to reduce fuel efficiency by 1%. This has led to interest in the use of cupronickel cladding on the hulls of merchant ships and warships[4,32] based on the proven performance of smaller vessels up to about 23 m LOA with monolithic cupronickel plate hulls. It is claimed and demonstrated that cupronickel hulls or cladding have inherent resistance to marine fouling, which results in fuel saving, more constant performance and savings in maintenance. Potential problems of bimetallic corrosion, sulphide filming in polluted waters and others related to fabrication have been considered and economic assessments have been made. However, in the recent period of recession no clad steel hull of significant size has yet been built, although pilot experiments employing clad rudders and 'patches' have been made.

Fairly extensive use of cladding has been made in the marine and offshore industry for the protection of the intermittently wetted tidal and splash zones of fixed steel structures in the sea. These areas cannot be effectively protected by either protective coatings or cathodic protection. 70/30 nickel copper sheathing has been used for many years for protection of piling and platforms in the Gulf of Mexico. In the North Sea where platforms are, in general, larger and in deeper water, sheathing has not been employed. In the gas field in Morecambe Bay where the platforms are in shallow water (about 30 m) but the tidal range is large, the jacket structures have been sheathed in 90/10 cupronickel.[4] The sheathing is 4 mm thick and extends from 4 m below the low water level to 13 m above. Tubulars up to 1.67 m diameter have been sheathed. The sheathing is attached to the steel structure by welding, which will result in some loss of antifouling properties since it will be protected by the sacrificial anode system attached to the steel structure. An alternative sheathing system, where the cladding would be insulated from the steel, was not considered practicable because of weight limitations. Sheathing or cladding with 70/30 nickel copper or 625 has also been used in the tidal and splash zones of hot oil riser pipes. Some use has been made of composite tubes for sour product lines employing a resistant stainless steel liner of up to 150 mm internal diameter fitted inside a carbon steel outer tube. Apart from weld fabrication problems, there seems no reason in principle why coextruded tubes should not be used for this and similar applications.



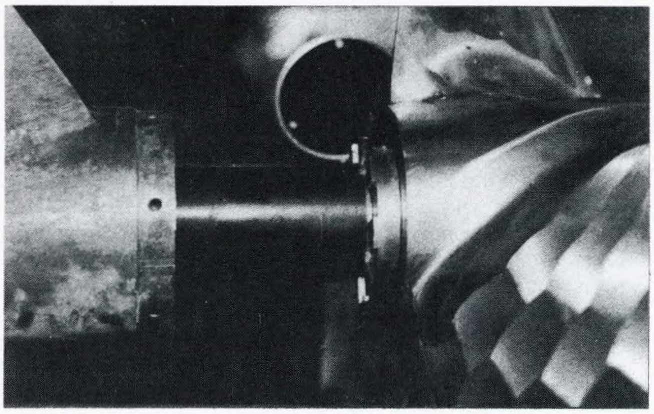


FIG. 14: Tailshafts: (top) Arc sprayed with copper–tin alloy and (bottom) Flame sprayed with chromium oxide

Thermal spray coatings or weld cladding have been employed by the Royal Navy for reclamation and repair and for tribological applications. Examples are given in Fig. 14, which shows a 3.5 m long by 540 mm diameter tailshaft reclaimed by the arc spray process using a copper tin alloy, and a K400 nickel copper tailshaft from a fast patrol craft coated with chromium oxide deposited by a gas wire spraying pistol using ceramic cord. The latter was to overcome wear in way of a mineral reinforced plastic bush in the 'A' bracket bearing area. Stabilizer fin shafts of En26 have been coated with 70/30 nickel copper by arc spray or with 625 by MIG welding.

Other potential novel uses of thermal spray coatings[4] include copper or 90/10 cupronickel coatings on concrete, GRP or wood and other non-metallic substrates to confer antifouling properties.

Hot corrosion in marine gas turbines has promoted the development by the Royal Navy of coatings possessing adequate resistance to both low and higher temperature corrosion.[38] Many of these are of the M–Cr–Al–X type, where M is usually cobalt for preference but can be nickel, and X is an element such as yttrium or zirconium. Co–Cr–Al–Y coatings developed in the USA were shown for the first time in rig tests at one of the UK naval research establishments in 1974 to have poor corrosion resistance at low temperatures, although they performed excellently above 800°C (Fig. 15). This was later confirmed in engines at sea. Subsequent research has established the merits of high chromium coatings with moderate levels of aluminium and an oxide stabilizing element such as zirconium which also appears to confer added resistance to sulphidation in preference to yttrium which, although effective as an oxide stabilizer, appears neutral in its effects on sulphidation.

## MISCELLANEOUS METALLIC MATERIALS

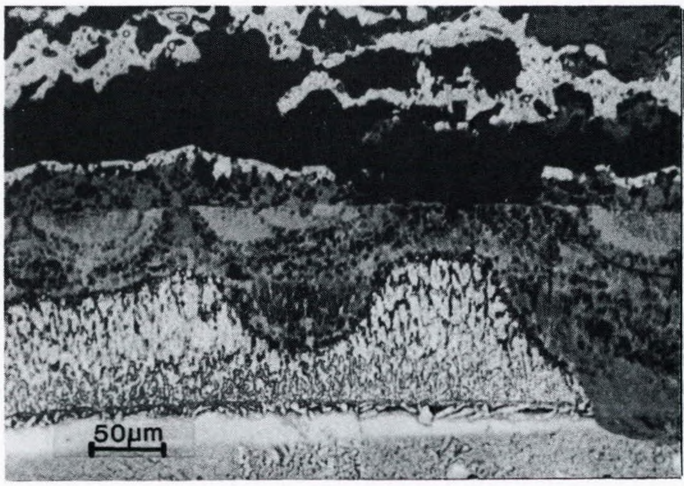
Certain novel materials have been developed in recent years which have found ready application in marine and offshore engineering. These include shape-memory alloys and materials for impressed current cathodic protection anodes.

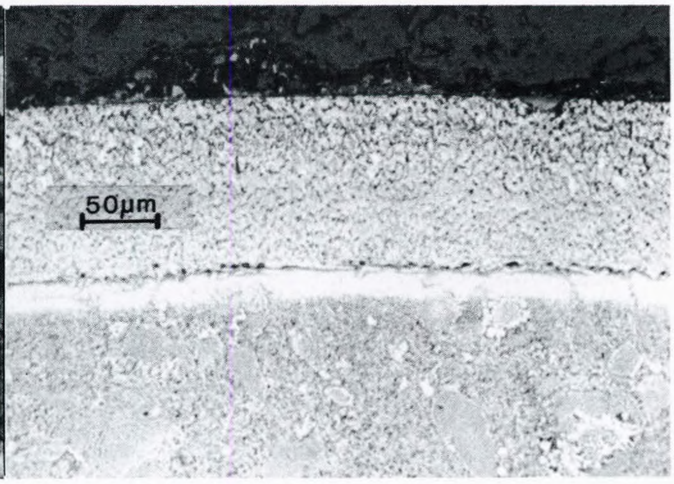
### Shape-memory alloys

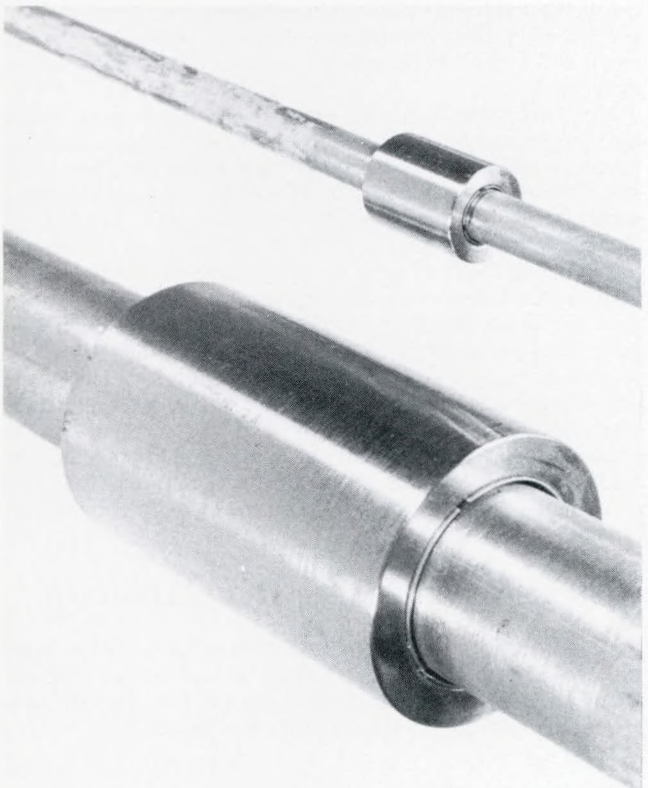
Shape-memory alloys or heat shrinkable metals are found in a number of alloy systems including Ni–Ti, Cu–Zn–Al and many others. Discussion of the mechanism of the shape-memory effect is beyond the scope of this paper but essentially these materials can be deformed easily at one temperature and then seek to resume their original form at higher temperatures, where they also become strong engineering materials.[39,40]

A particular application in the Royal Navy and also in the offshore industry has been in initial joining of small diameter pipework where access for welding is limited or for repairs on pipes in confined or hostile environments. Pipe couplings can be monolithic or can have a liner (Fig. 16), for example a cupronickel alloy, for joining cupronickel pipes to minimize crevice and bimetallic effects. To prevent corrosion in some particularly hostile environments the couplings can be protected by heat shrinkable plastic sleeves, which can be slipped on to the pipe before installing the coupling and subsequently located over the shrunk-on coupling and shrink fitted. For

FIG. 15: Co–Cr–Al–Y PVD coatings rig tested at (left) 750 and (right) 830°C





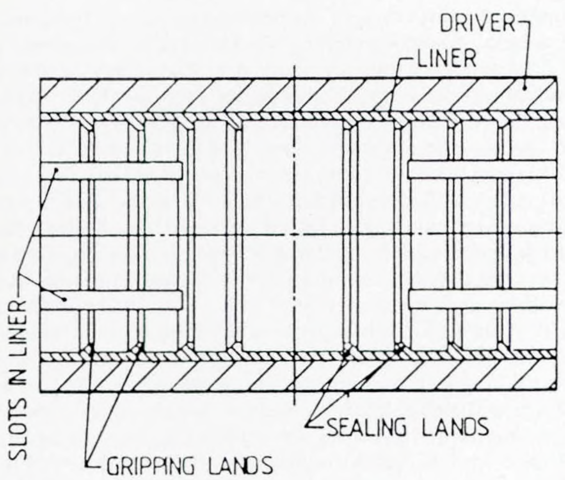



**FIG. 16: Shape-memory alloy pipe couplings**

installed couplings where the plastic sleeves cannot be fitted, wrap around, 'zip-up' sleeves are available.

### Anodes for impressed current cathodic protection

In recent years there have been significant advances in anode materials for impressed current systems. Platinized titanium or niobium anodes have been used for about 25 years as high current density (about 500 A/m$^2$) inert anodes. To improve life and performance under aggressive conditions (e.g. acid conditions, abrasion or mud), single or multiple precious metal oxide coating systems have been developed.[41] These consist of iridium and ruthenium oxides which may be deposited directly on to titanium or niobium or on to tantalum sheathed titanium or niobium. For particularly abrasive conditions, a porous electrically conductive titanium oxide based ceramic is used as coating and this is impregnated with the precious metal coating. A whole family of such materials exist and show particular attributes, hence selection must depend on prevailing circumstances and economic factors.

## CONCRETE

Whilst concrete has been used extensively for fixed installations, some offshore platforms, boats, barges for towable process plant (e.g. desalination plants) and a whole variety of other marine applications, the introduction of potentially superior, but more expensive, materials tends to be economically unattractive owing to the sheer volume of material in many applications. There is interest in Scandinavia, the USA and elsewhere in lightweight concrete which uses pulverized fuel ash (PFA) which is ground or sintered to produce lightweight aggregate. Strength equivalent to normal marine grades of concrete can be achieved with only 80% of the density. There is some interest in its use as an impact resistant material to absorb damage from dropped objects. It also has better thermal insulating properties than normal concrete. In the event that natural aggregate increases in cost then PFA could become of greater interest.[42]

The use of alkali resistant glass or polypropylene fibre reinforced concrete and steel wire reinforced materials is of interest for manhole covers but cost prohibits more widespread use. The recently developed macro-defect-free (MDF) cements, with compressive strengths greater than 200 N/mm$^2$ and flexural strengths of around 60–70 N/mm$^2$, are attractive materials and may have some specialized applications but again cost, as well as possible difficulty in attaining a good bond between successive pours, may preclude quantity use.

## COMPOSITES

Considerable use has been made of GRP in marine applications and glass fibre remains the preferred reinforcement in most commercial applications. A few racing craft have been constructed employing carbon fibre reinforcement but this is too expensive for other than specialized use. Kevlar fibre is of greater interest but adds about 14% to the costs in comparison with GRP and is reputed to be more difficult to work with than glass. However, it is claimed to provide better fuel economy. Hybrid materials with mixed glass/Kevlar or glass/carbon fibre reinforcement are of some interest for specialized applications where greater lightness or stiffness is essential. There have also been developments in the thermosetting matrix resins to achieve faster cure and other characteristics. A further significant development has been polyester resin with photoinitiators which enable rapid curing by light and which can be used to preimpregnate reinforcement. In addition to these developments there have been others in thermoplastics matrix materials, together with fibre mats, woven fabrics and triaxial materials, and other fibre forms. Some of these improvements will find application in marine composites.

A novel application of carbon fibre reinforced plastics is in aluminium alloy structures to arrest fatigue crack growth by use of an adhesive patching technique to spread the loading.[43] Similar techniques are possible for marine aluminium alloys, where weld repair of fatigue cracks may not be effective and prompt reinitiation may occur. Clearly in the marine environment care has to be taken to avoid galvanic corrosion due to exposure of the carbon fibres, and coatings to ensure insulation and protection from mechanical damage are essential. Other inert fibres are potentially more suitable for use in marine structural patching.

A great deal of research is in progress in the USA, Europe and elsewhere on metal matrix composites for lightweight stiff structural applications. Certain of these materials may be of interest for high technology marine applications. Fibres for reinforcement which are under investigation include carbon fibre, alumina and silicon carbide, and also whiskers of various types. Currently research is concerned largely with aluminium alloy matrices but other matrices are potentially possible in the longer term.

## ORGANIC MATERIALS

Considerable development in paint technology has taken place in the last decade. Lead based paints have been replaced, including red lead primer which had been one of the main anticorrosive primers used on ship hulls for most of this century. This has been dictated by environmental and health and safety requirements and zinc phosphate has been used as a replacement. Efforts have also been made to improve the life of organic coatings to reduce the maintenance load. In the Royal Navy, silicone alkyd weatherwork paints are being evaluated on ships in the fleet in order to select a coating with improved gloss retention properties, thereby discouraging repainting of large areas where touch-up would suffice.

Undoubtedly one of the most significant developments in paint coatings in the past decade has been the introduction of the commercial erodable or 'self polishing' antifouling paints.[44] The most common biocide used is tributyltin oxide attached to an acrylic polymer as TBT carboxylate, which was the main biocide in the original paints of this type. More recent formulations have increasing levels of cuprous oxide or cuprous thiocyanate as additional biocides. These modern types of antifouling paint are claimed to be inherently much safer to handle and are less toxic than traditional antifouling formulations. They provide a controlled release of biocide into the surrounding seawater for as long as the coating remains.

The chemistry of these materials is beyond the scope of this discussion but on release of the toxin into the water the polymer itself becomes water soluble and dissolves, exposing fresh biocidal polymer. The most recent developments include higher solids coatings which permit thicker films to be applied in a single coat, i.e. high build coatings. In addition, 'polishing' rate can be adjusted to suit the type of ship operation; e.g. faster polishing, higher biocidal, systems are appropriate for low activity ships with long stationary periods, whilst slower acting coatings are suitable for quick turn-round vessels. These erodable antifouling paints also overcome the problem of 'drying out' due to jamming of the skeleton, which is common to conventional antifouling paints when they have been in use for some time and are allowed to dry out. The 'self-polishing' materials also have predictable life with given operating conditions. In warship applications, lives in excess of 4 years have already been achieved. They have provided one approach to improving ship operating efficiency in a decade when fuel costs have escalated rapidly.

An alternative commercial development in the antifouling field has been the discovery of coatings based on rubbers, where the surface properties inhibit fouling without recourse to toxins. Raft trials of these modified silicon rubbers indicate a useful life of at least 10 years.[45]

Other antifouling rubbers have been evolved containing TBT compounds and other toxins, which all have some solubility in the rubber and can diffuse through the rubber matrix to reach the rubber/water interface. The rubber structure is not affected significantly by release of the toxins into the water and maintains a smooth surface. These coatings have the advantage that they can be relatively thick compared with paints and hence the effective life of commercially available materials should be greater than that of a paint system.[45]

Polymeric coatings have also been developed in the past few years for impact, abrasion and erosion resistance as well as providing corrosion protection. These can be of a number of different types[46] including thin film solvented epoxy systems, solvent-free epoxy systems, glass flake filled epoxies and polyesters and elastomeric coatings such as polyurethane. In general, the solvented and solvent-free epoxies show reduced impact resistance as film thickness increases; glass flake materials show little thickness dependence, and elastomeric materials show increased impact resistance with greater thickness. Thicknesses are usually 0.3 mm for solvented epoxies, 0.5 mm for solvent-free epoxies, 0.5–1.0 mm for glass flake materials and 1.0–3.0 mm for elastomeric coatings. If required, elastomeric coatings can be applied up to 50 mm thick and in general offer excellent resistance to abrasion and impact and are very effective barriers to water.

Applications of solvent-free epoxies include hulls of ice-breakers and other vessels operating in ice, whilst glass flake materials are used on the splash zones of oil rigs and platforms. The elastomerics have been used on hovercraft propeller blades, protection of condenser boxes for marine steam turbines and desalination plant, wear resistant coatings for concrete decking and impact resistant coatings for the sides of barges. Relative costs are: solvented epoxies 100, solvent-free epoxies 170, glass flake materials 150, elastomerics 600. However, in terms of relative cost for equivalent lifetime against erosive wear these become: 100/160/200–400/20 based on dry film thicknesses of 0.3/0.5/0.5/3.0 mm respectively.

A novel application of adhesives has been development of techniques for repair of water and oil contaminated structures which has entailed development of suitable underwater adhesives and surface conditioning procedures.[47] The surface cleaning/preparation method involves the deposition of a so-called 'preferred contaminant' which endows the surface with a temporary water repellent quality but which is receptive to the adhesive. The technique can be applied to steel, GRP and possibly other materials, i.e. steel to steel, GRP to GRP.

## CERAMICS

Many marine engineering problems arise owing to bimetallic corrosion effects in seals and bearings operating in seawater or marine environments. Frequently problems are incorrectly attributed to shortcomings in tribological performance when the root problem is corrosion or corrosion debris. In addition, in marine environments seals and water-lubricated bearings may need to resist erosion by sand and other abrasive materials. Certain of the cobalt bonded carbides may be subject to leaching of the cobalt in seawater and loss of strength and performance. A variety of strong ceramic materials which are inert in seawater and do not induce galvanic corrosion effects in mating or housing materials are available for arduous applications. Sintered alpha silicon carbide is one such material and there is a whole family of silicon based ceramics, all of which have particular attributes of strength and relative cost as well as varying in tribological properties. These include the various forms of silicon nitride (reaction bonded, sintered, hot pressed) and sialons as well as the silicon carbide variants of which there are many. In addition there are the various forms of carbon and graphite, many of which have been utilized in marine seals but which are more noble in seawater than most engineering materials and may induce galvanic corrosion.

The use of thermal spray ceramic coatings, such as chromium oxide for tribological applications in seawater, has been discussed earlier and it has been found that by depositing the coating on a crevice corrosion resistant intermediate coating such as 625 good performance can be obtained.

A great deal of research and development world-wide is devoted to the use of monolithic ceramics or ceramic coatings in engines of all kinds with a view to enhancing efficiency, overcoming corrosion and erosion problems and generally improving reliability under onerous conditions. A proportion of the effort is devoted to refractory fibre reinforced ceramics which have enhanced toughness compared with monolithic ceramics and this may help to overcome some of the natural reluctance of engineers to employ inductile but strong ceramics. Undoubtedly in the future more applications for ceramics will evolve in marine and offshore engineering, since the raw materials are cheap and readily available and are not likely to be subject to resource politics. Ceramics also have the advantage of low density and, in the long term, low cost.

## DISCUSSION AND CONCLUSION

In spite of the wide range of new materials and new applications for established materials in the marine and offshore industry, there are still some areas of opportunity where no fully satisfactory materials have yet been found. Two specific examples have arisen because of environmental and health and safety requirements. These are adequate substitutes for cadmium plate for fasteners and for chromate inhibiting primers for aluminium alloys. A great deal of research and development in the past few years has failed to produce a fully satisfactory protective coating with all the many attributes of cadmium, particularly for electronic components and fasteners. Whilst inhibitors have been identified (e.g. glycollates) which appear as effective as chromate, they are unfortunately incompatible with certain primers such as epoxies.

However, isolated but important instances of this kind apart, given the requirement and incentive it is clear that viable solutions can be found to materials problems in the structural and engineering areas of the marine and offshore industry. The final arbiter in selection of new materials is performance and economics. In general the costs of repair of adventitious failures and the penalties of consequential damage must be added to the loss of availability or product and new and improved materials, although showing higher first costs, may ultimately ensure lowest through life costs or costs of ownership. Clearly, choice of new materials must be based on sound technical and economic assessment as well as good engineering judgement.

## ACKNOWLEDGEMENTS

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# Discussion

**V. A. CALLCUT** (Copper Developments Association): Can you recommend a suitable adhesive for fixing cupronickel foil to GRP hulls?

**T. J. GLOVER** (Inco Europe Alloy Products Ltd): Three fireboats have been built in Italy for the Department of the Interior using cupronickel clad plate. They were the first such vessels to be built on a purely commercial basis. If successful, a further 8 will be built. The use of clad plate is the most economic and technically sound technique for applying cupronickel to the outside of a craft.

**B. TODD** (Inco Europe Alloy Products Ltd): In his presentation, the author stated that the ferritic stainless steels developed crevice corrosion resistance equivalent to the austenitics but at a lower molybdenum content. Could he clarify this? Does he mean that the ferritics have this inherent property or does he mean that the higher chromium content of the ferritics compared to the austenitics (26% cf. 20%) allows a lower molybdenum content to be used.

The author states that weldments of nickel aluminium bronze are prone to selective phase corrosion in the heat-affected zone. Is there any way of avoiding or eliminating this on weldments in this alloy?

**H. CAPPER** (Consultant): Mr Condé has dealt with a very wide range of materials for use in a marine environment and although materials for use in cathodic protection systems have been mentioned, the effect of such systems on the choice of structural materials in a corrosive environment has not. I would like particularly to draw attention to the ameliorating effect of cathodic protection on damage by corrosion fatigue. It is true to say that wherever fluctuating stresses are at work in a marine environment, any resultant cracking is due to a corrosion fatigue process. The application of cathodic protection in such conditions prevents, or at worst delays, the roughening of the metal surface due to corrosion from which such cracks are initiated. That this will be the case where stresses are low and the time factor long is fairly obvious, but I have experience of severe cracking in a ship's plate being acceptably delayed in ballast tanks where crackng was experienced in months due to high applied stresses in service before cathodic protection was fitted. This leads one to the conclusion that higher strength steels could be used in shipbuilding with consequently higher service stresses and weight saving. Furthermore, internal stress due to welding may not be so damaging provided cathodic protection is efficiently provided.

I would also like to add something on the virtues of titanium alloys in corrosive conditions. Two examples are worth mentioning. In a dust collector in the uptake from a marine boiler the conditions comprised hot sulphurous gases at about 160 °C in a salt-water spray; commercial grade titanium sheet was only tarnished after 3 years. In a rotary air preheater where metal sheets are alternately subjected to salt-laden cold air and hot furnace gases, titanium sheet was unaffected but a variety of other materials were severely corroded.

More information on the surface treatments which can be obtained by ion implantation would be interesting. I believe this process will yield significant changes in corrosion resistance, tribology and many other useful applications in the near future.

Thanks are due to the author for a most interesting paper.

**J. L. CLARKE** (Cement and Concrete Association): Mr Condé's paper touches briefly on the use of concrete for marine structures. It should be stressed that concrete, unlike steel, is largely maintenance free if correctly made in the first place. This could be a significant factor when choosing the material for a fixed or floating structure in hostile waters, such as the North Sea or the Arctic. As an example, the concrete base of the Nab Tower, installed in the waters of the Isle of Wight in 1919, was surveyed recently and found to be in almost perfect condition. Turning to the future, there is indeed growing interest in the use of lightweight aggregate concretes, particularly for marine structures for the Arctic. There are in fact a number of suitable lightweight aggregates, those made from pulverized fuel ash (PFA) being only one type. The statement that '. . . if natural aggregate increases in cost then PFA could become of greater interest' is slightly misleading. PFA is also used, in its original form, as a cement replacement, but this will lead to a concrete of normal density.

# Author's Reply

In reply to Mr Callcut's question about the attachment of cupronickel foil to GRP hulls to provide antifouling characteristics, there are a number of problems including the fact that copper inhibits certain organic adhesive systems and hence the choice of adhesive is restricted. The adhesive also has to be 'gap filling' so it needs to be of the thermosetting type; these materials require time to set and hence the cladding/resin system has to be held in place whilst the resin cures. A further important factor is the durability of the adhesive/metal interface in fresh or sea water.

The most attractive approach would be to apply a cold-curing epoxy resin system in conjunction with the use of a proprietary 'primer' applied to the bonding surface of the cupronickel foil. Such primers may need to be applied under workshop conditions since they normally require heating at 100 °C or slightly higher. A number of underwater adhesive systems such as UW43 and UW45 have been developed at ARE, Holton Heath which would be suitable for bonding to GRP. Suction pad devices could be employed to hold the foil in place while cure takes place.

An alternative approach to using cupronickel is a proprietary polymeric tile or sheet which contains chips of antifouling material in a rubber matrix. This tile or sheet material can be readily bonded to GRP.

The question of the relative crevice corrosion resistance of the austenitic and ferritic stainless steels under sea water and other high chloride aqueous exposure conditions is complex and depends, as Mr Todd suggests, on not only molybdenum content but also chromium and nitrogen levels. Resistance to pitting and crevice corrosion is mainly a function of the combined chromium and molybdenum contents but nitrogen also has a beneficial effect. However, in the ferritic stainless steels nitrogen has detrimental effects on toughness and weld sensitization and hence resistance is conferred by a high level of chromium and a level of molybdenum commensurate with freedom from undesirable additional phases in the microstructure.

In the austenitic stainless steels high chromium and molybdenum levels increase the tendency to form the undesirable sigma phase and raising the nickel content in an attempt to overcome the problem may not be a satisfactory technical solution and may increase costs. Thus in many crevice corrosion resistant stainless steels performance is achieved by maintaining the chromium level at about 18–22% and employing a higher molybdenum content compared with the ferritics. Performance is further enhanced by the presence of 0.1–0.2%

nitrogen, which serves to enhance not only corrosion resistance but also mechanical properties and the ability to make welds in heavy sections of up to 50 mm without significant degradation due to sigma-phase formation.

There are at present no known fully practical ways of avoiding the problem of selective phase corrosion of the heat-affected zone (HAZ) in weldments in cast nickel aluminium bronze subjected to long-term exposure to sea water. The problem is not peculiar to weldments and can occur in cast parent material since it is related to selective phase corrosion of the kappa III phase under crevice conditions. However, the corrosion may be more significant in a weldment since the HAZ may be continuous through the wall thickness and lead to penetration and leakage.

The kappa III phase occurs as a continuous lamellar or rod-like phase which can be spheriodized by heat treatment at about 900 °C or higher. However, such treatments are not practical on large cast shapes or machined components because of distortion. If applied they would need to be carried out at the pre- or part-machined stage of manufacture. Lower temperature treatment is not effective. Use of laser heating to locally treat the sea water wetted surfaces of parent material and HAZs is being examined in an attempt to modify the kappa III phase in the near surface region. This may provide a possible solution but even if successful its practicality in a realistic manufacturing environment would need to be established.

Mr Capper's comments on the influence of cathodic protection on corrosion fatigue resistance particularly of steels is of considerable interest and, as he suggests, the technique has been used successfully in a variety of circumstances. However, it is only likely to be fully effective when the whole structure is wetted by the sea water electrolyte and where the potential can be maintained uniformly. This latter condition may be difficult to achieve due to the geometry of the structure and throwing power effects which are sensitive to geometry. If local high-stress regions happen to coincide with areas of over protection then fatigue crack growth rates may be enhanced.

Research on low alloy steels such as HY80 has shown that at −700 mV (vs SCE) environmental contributions to crack growth are attributable to dissolution processes whereas at −950 mV (vs SCE) increased crack growth rates can only be attributed to hydrogen embrittlement. Other studies elsewhere[1] on BS 4360 Grade 50D have shown that on tubular joints in which crack initiation and propagation were measured, sea water and sea water with cathodic protection showed different effects in spite of the fatigue lives being equal. Thus it is not a safe assumption that higher strength steels can be used in ship construction and protected from corrosion fatigue by cathodic protection.

Regarding the use of titanium in uptakes and other corrosive environments another successful application has been for diesel exhaust uptakes in GRP mine countermeasures vessels.

Ion implantation is currently a rapidly developing technology and in the marine environment an attractive possibility is the use of implantation of stainless steels with molybdenum to improve the local crevice corrosion resistance of items such as fasteners. Implantation with nitrogen to improve the corrosion resistance and tribological performance of high duty rolling bearings is a further area offering potential benefits.

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1. T. W. Thorpe *et al.*, 'Corrosion fatigue of BS 4360: 50D structural steel in sea water'. *Int. J. Fatigue*, Vol. 5, No. 3 (July 1983).

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