Nickel in non-ferrous general engineering alloys

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ALTHOUGH nickel in its wrought forms has important applications as an engineering material, particularly in the chemical and electronic industries, the major usage of the metal, in both ferrous and non-ferrous metallurgy, is as an alloying element.

Nickel-base alloys can be broadly divided into the nickel-chromium-base "Superalloys" for high-temperature service, and materials, such as nickel-copper and nickel-chromium-iron alloys, which are used for more general engineering purposes, particularly where resistance to corrosion is involved.

The technology of the former type of material tends to be rather specialized, since it is concerned very largely with high-temperature properties, and it is not proposed to discuss these high-temperature alloys in this paper but to describe some recent developments in the nickel-base alloys of general engineering interest and in the nickel-containing copper-base and aluminium-base alloys.

Alloy 625

A nickel-chromium-molybdenum alloy, the nominal composition of which is given in Table I, has been developed in recent years in the U.S.A. as a high-temperature material. It is now finding application in this field, but other uses which depend on wet corrosion-resistance are under active investigation.

Alloy 625 has excellent resistance to many aqueous environments, including chloride mixtures, but of particular interest is its extremely high resistance to sea-water corrosion. The general corrosion rate of the alloy under all conditions of exposure is for all practical purposes zero ; even in crevice conditions it is extremely resistant to the pitting attack in sea-water which occurs in many high-chromium alloys. It has shown high resistance to stress corrosion in all tests carried out to date. This corrosion-resistance coupled with excellent strength, makes the alloy of considerable interest in marine engineering applications.

In wire form alloy 625 can be cold drawn to tensile strengths in excess of 210 kg/mm^2, and can therefore be used to produce marine wire rope of outstanding properties. Wire at this strength level has been made into wire rope 6·3 mm in diameter and comprising seven strands of 19 wires each. The breaking load of this rope was approximately 3·500 kg.

Corrosion tests have been carried out on this alloy 625 marine wire rope fully immersed in flowing sea-water, partially immersed in sea-water, in the tidal zone with alternate wetting and drying and in mud on the sea bed. In one test the wire rope is being immersed in sea-water at a constant depth just below the surface. Three samples were exposed in September 1966, and Fig. 1 shows these three pieces of rope after one year. It will be noted that consideraable fouling has taken place. One length of rope was taken out at this inspection, and the fouling removed by brushing. Fig. 2 shows the condition of the surface after this removal of fouling. Tensile tests were then carried out, and the breaking load was exactly the same as for the rope before exposure, i. e., 3500 kg. The remaining two samples are being given two - and three-year exposures before being examined.

Stress-corrosion tests on full sections of rope are

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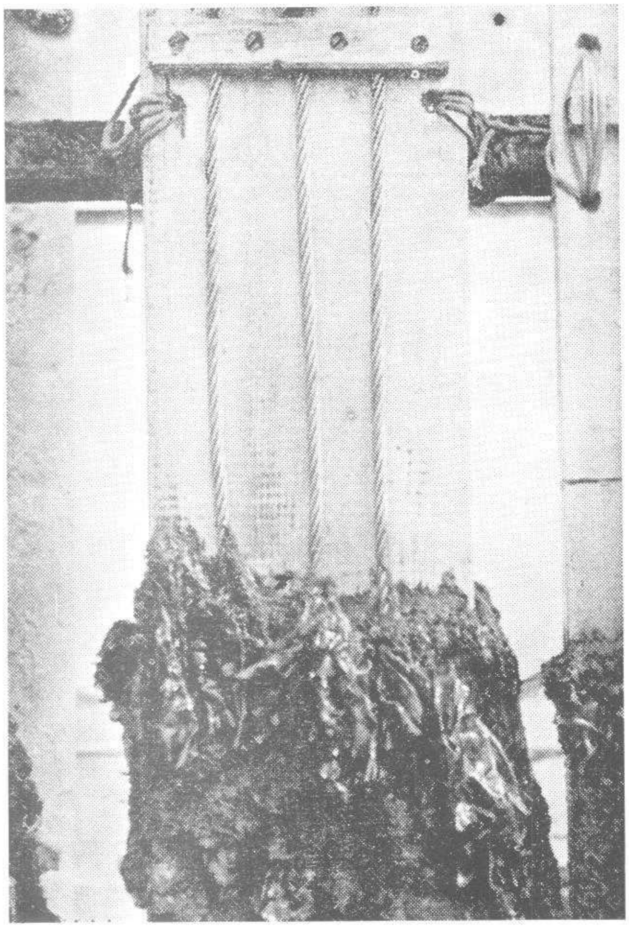
SYNOPSIS

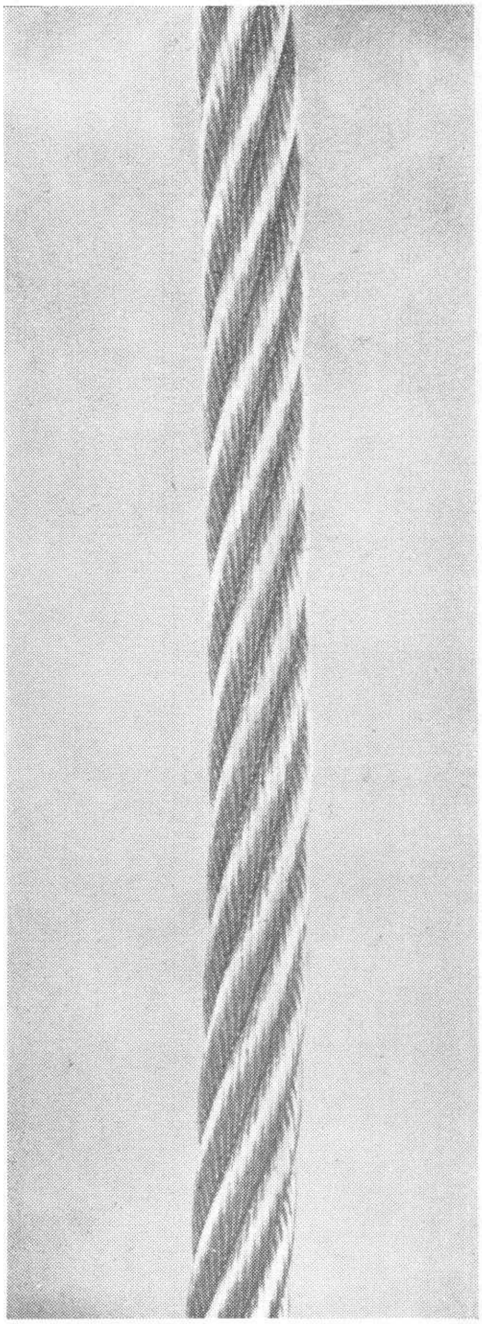
Some recent devolopments in the nickel-containing copper and aluminium alloys and in nickel alloys of general engineering interest, i.e. excluding the high-temperature alloys, are described in details in the paper.

TABLE I Nominal composition of alloy 625

Element	Per cent
Chromium	22
Molybdenum	9
Niobium (+ tantalum)	4
Iron	3
Nickel	Balance



1 *Alloy 625 wire ropes after one year immersed in sea-water showing method of suspension and marine fouling of submerged portion*



2 *Alloy 625 wire rope after one year immersed in sea-water; this shows part of the submerged portion after marine fouling had been removed by brushing*

now also in progress in sea-water exposures. These tests are being carried out in specially designed rigs which maintain a stress on the wire rope equivalent to 90 per cent of its breaking load. So far, no failures have occurred in three months' exposure, but the tests are continuing.

The corrosion-fatigue properties of alloy 625 in sea-water have been determined for material in bar form. The stress for failure after 100 million cycles was ± 35 kg/mm^2—probably the highest value obtainable from any commercially available material so far. Further tests are in progress to determine the fatigue properties of wire rope in sea-water at about 10 cycles per minute, to simulate service conditions. These have so far indicated that there is no reduction in strength or life in sea-water compared with similar tests in air.

The applications which are envisaged for alloy 625 marine wire rope are mostly concerned with oceanographic work. The alloy is, of course, relatively expensive when compared with galvanized or aluminized steels, but it is believed that the extra cost is likely to be justified where long-term reliability is necessary, as when expensive instruments are to be moored in sea-water for long periods.

Nickel-silicon alloys

Nickel-silicon alloys containing about 10 per cent silicon have been in commercial use for a considerable time as castings resistant to sulphuric acid attack.

TABLE II Typical tensile properties of some high-strength cupro-nickels

Alloy	Composition (weight per cent) Ni	Fe	Mn	Other	Form	Tensile strength kg/mm²	0·2% proof stress kg/mm²	Elongation
'Hiduron' 191	17	1	5	1·75 Al	As-rolled bar	75	47	32
Nickel Bronze NBI	14·5	—	—	2·5 Al	Heat-treated bar	125	45	10
717C	30	0·7	0·8	0·45 Be	Heat-treated casting	82	58	15

However, the use of these alloys in boiling sulphuric acid is limited to concentrations below about 80 per cent; above this acid concentration the rate of attack tends to be very rapid. The only material which will withstand boiling sulphuric acid throughout the whole concentration range is silicon-iron containing about 14·5 per cent silicon. This alloy suffers the disadvantage of being extremely brittle, which tends to increase the initial cost, to make it necessary to design components with heavy sections and generous radii, and to involve risk of sudden failures in service.

Recent work on ternary nickel-silicon-titanium alloys has led to the possibility of developing an alloy which will combine good resistance to boiling sulphuric acid throughout the whole concentration range with a useful degree of ductility. This work has established that the beta phase of the binary nickel-silicon system is more ductile than previously supposed, and that titanium additions stabilize this beta phase. The corrosion-resistance of the nickel-silicon-titanium alloys having essentially a beta structure can be further improved by additions of molybdenum and copper. Alloys of this type have already been patented.[1] As an example of the behaviour of these materials in boiling sulphuric acid, an alloy containing 10 per cent silicon and 3 per cent each of titanium and copper exhibited a corrosion rate substantially below 100 mdd in acids of 25, 75 and 90 per cent concentrations. The corresponding corrosion rate of a similar alloy without the titanium was in excess of 700 mdd in 90 per cent acid. The elongation of the 10%silicon-3%titanium-3%copper alloy in a room-temperature tensile test was 1·1 per cent in the as-cast condition, but 4·5 per cent after annealing for 16 hours at 1050°C.

Development of these alloys is still in progress; coupons of the most promising compositions are being exposed to process streams to evaluate the effects of impurities in the acid and some small trial castings have been made. Results to date indicate that a new material of this type will shortly be available for use in the production, use and recovery of sulphuric acid in the chemical, petrochemical and process industries.

High-strength copper-nickel alloys

The copper-nickel alloy containing 10 and 30 per cent nickel, modified with small additions of iron and manganese, have been important materials for marine engineering applications for many years. Their chief use has been in heat-exchanger applications, such as condensers in steamships and coastal power plants and in large land-based desalination plants, the latter being of particular importance in recent years. For most of these applications the moderate strength of these cupro-nickels have been quite adequate, but there has been an interest in using alloys of these types in a wider range of applications, which has led to the development of several high-strength alloys.

Some of these high-strength cupro-nickels are already commercially available in the U.S.A. and Europe, and the compositions and properties of three of these are summarized in Table II

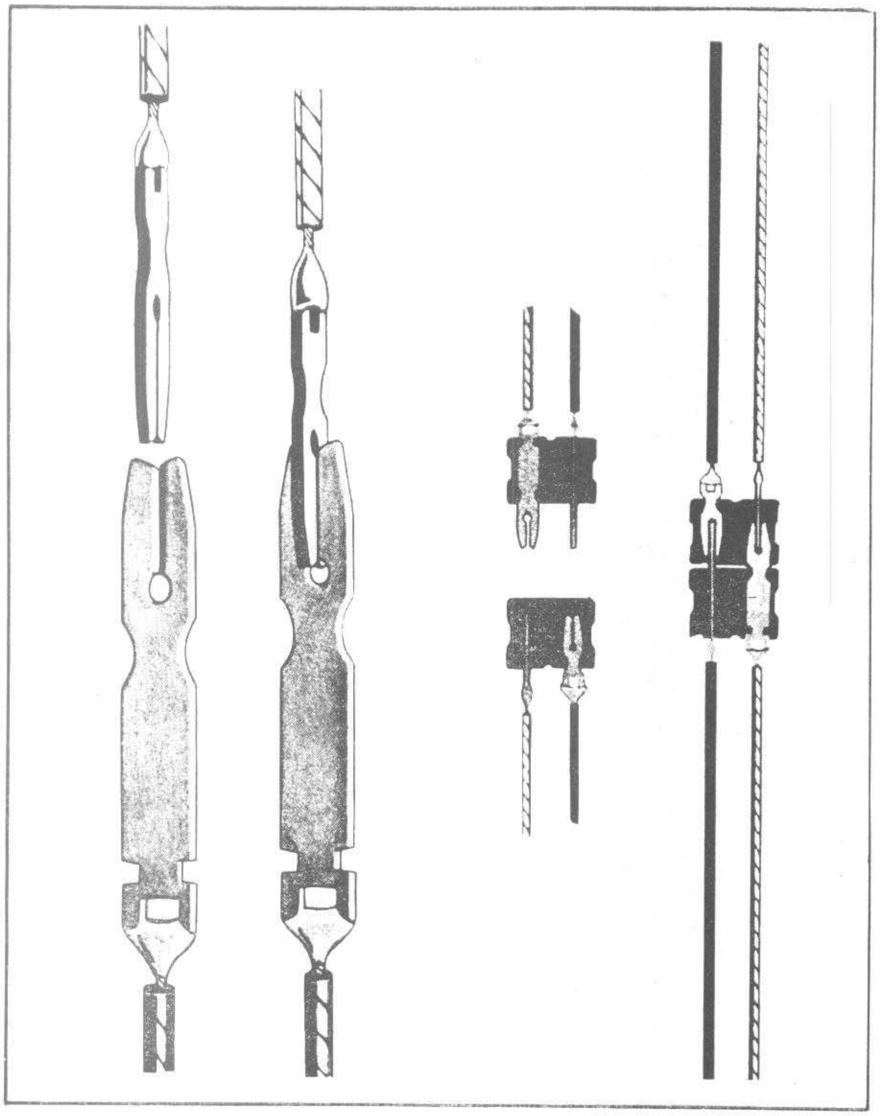
These three alloys are already being produced commercially ('Hiduron'* 191 in the U.K., Alloy 717C in the U.S.A. and nickel bronze NBI in Germany) and all are essentially precipitation-hardening alloys, although separate heat-treatments are carried out only if the maximum level of strength is required.

Another cupro-nickel of enhanced strength has recently been invented and is in the process of being developed commercially. This alloy, IN-732-X, is unusual in that the strengthening mechanism is a spinodal decomposition. The composition of IN-732-X is shown in Table III.

TABLE III Nominal composition of alloy IN-732-X

Element	Per cent
Nickel	30
Chromium	2·8
Iron	0·2
Manganese	0·7
Zirconium	0·15
Copper	Balance

*Trade Mark



3 *New design of electrical connector, using nickel silver as described by Worth*[3]

The spinodal decomposition occurs below 760°C during cooling from the annealing or hot-working temperature and requires less than ten seconds to take place. Air cooling of sections of about 1·5 mm is sufficient to cause full hardening, and in thicker sections the reaction cannot be fully suppressed, even by quenching. The mechanism of the reaction has been described by Badia, Kirby and Mihalisin.[2] Briefly, the alpha face-centred-cubic phase, which is stable at high temperatures, becomes unstable as it cools and tends to separate into two new alpha phases very closely related in lattice parameter with very little difference in composition. Because this reaction is controlled by diffusion over very short atomic distances and not by nucleation, the reaction appears to be almost instantaneous and occurs simultaneously throughout the section during continuous cooling. The hardening is attributed to coherency effects between the two alpha phases. Very slow cooling does not embrittle or change the structure of the alloy, although some increase in strength is evident.

Typical mechanical properties of annealed strip about 6 mm thick are: tensile strength, 60 kg/mm^2; 0·2% proof-stress, 37 kg/mm^2; elongation, 32%. The strength may be increased by cold-working operations, and material cold-rolled 90 per cent, for instance, can attain a proof-stress of about 85–90 kg/mm^2.

Preliminary studies indicate that IN-732-X is fully weldable by conventional techniques with little or no loss of strength at the weld or surrounding areas, but the development of the most suitable filler materials is not yet complete.

The alloy has essentially the same corrosion characteristics as the standard 70/30 cupro-nickel containing iron, except that it is rather more resistant to impingement attack in rapidly-flowing sea-water. It is of interest to note that the iron content of about 0·7 per cent which is necessary to minimise impingement attack in the standard alloy is not necessary in the high-strength material, the chromium appearing to substitute for iron.

IN-732-X is not yet in commercial production, although trial heats have been made under commercial conditions.

The alloy is currently being evaluated by a number of potential users for high-strength corrosion-resistant components in marine engineering. One interesting potential application is in the rapidly growing area of ocean engineering, where it could find use for fasteners, fittings and instrument housings.

Nickel silvers

The other class of copper alloy in which nickel is a major alloying element is the one of nickel silvers. These are, of course, very old-established materials, but they have been used largely for decorative applications, such as spoons and forks, holloware and architectural trim. The only major use in general engineering has been in the telecommunications industry, which uses the copper-18% nickel-27% zinc alloy in particular for relay springs and contacts.

The engineering properties of the nickel silvers have been the subject of renewed interest recently, and the alloys are being increasingly used for springs and connectors in the electrical and electronics industries. In one example of this, recently described by Worth[3], the alloy containing 12% nickel and 29% zinc has been used for a new design of connector, as shown in Fig. 3.

This interest in nickel silvers as engineering materials has led to laboratory investigations into their mechanical and physical properties, with particular attention to the characteristics of CuNi18Zn27 and CuNi12Zn25, the alloys most used by the telecommunications industry to date.

The elastic moduli in tension and in torsion of these two alloys have been determined over the temperature range 20 to 300°C, and these are shown in Tables IV and V.

TABLE IV Elasticity data for CuNi18Zn27

Temperature °C	Modulus of elasticity (kg/mm^2) In tension	In torsion
20	13 900	4 900
100	13 200	4 700
200	12 600	4 600
300	11 550	4 800

For spring applications CuNi18Zn27 is normally cold-rolled to a temper corresponding to a Vickers Hardness of about 240; in the case of CuNi12Zn25 a slightly less hard temper is used, corresponding to a Vickers Hardness of about 210. Tensile properties for the two alloys in these tempers have been determined at 20°C, 100°C and 200°C, as shown in Table VI.

TABLE V Elasticity data for CuNi12Zn25

Temperature °C	Modulus of elasticity (kg/mm^2) In tension	In torsion
20	13 100	4 270
100	12 750	4 200
200	12 500	4 130
300	12 000	4 060

TABLE VI Elevated temperature tensile properties of CuNi18Zn27 and CuNi12 Zn25

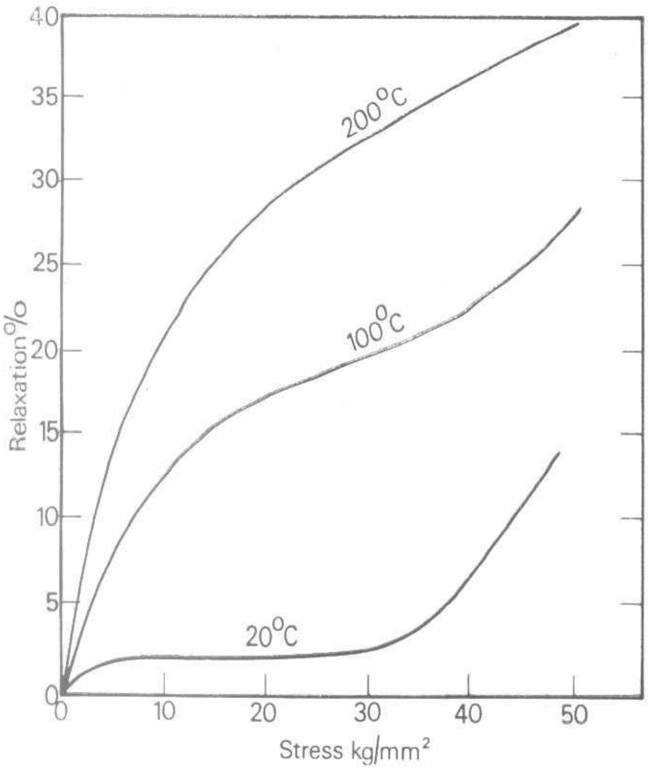
Alloy	Temperature °C	Tensile strength kg/mm^2	0·2% proof stress kg/mm^2
CuNi18Zn27	20	81·5	73·5
	100	79·8	76·5
	200	78·4	76·7
CuNi12Zn25		67·7	66·0
		66·6	65·5
		65·0	63·3

It will be noted that, in these short-time tensile tests, the strength properties are unaffected up to 200°C, which is likely to be the maximum working temperature of electronic or electrical components in these alloys.

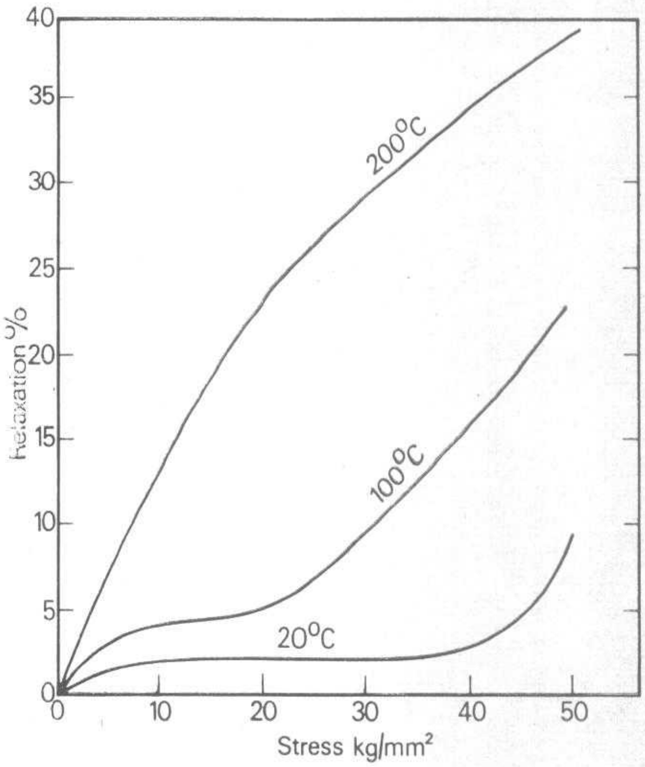
Stress relaxation is an important property of both spring and connector materials, and tests have been carried out at temperatures up to 200°C. These tests were conducted by bending strip specimens to a fixed radius of curvature, such that all the strain was elastic, exposing to the test temperature for a period of time, and then removing the specimen from the rig and computing the amount of elastic strain that was converted to plastic strain.

Relaxation curves for the two alloys in question are given in Figs. 4 and 5.

Other properties of interest to the designer of electrical contacts and springs are fatigue strength and contact resistance, both of which are being examined. With regard to the latter property, however, it is worth noting that, because the nickel silvers are



4 *Stress-relaxation curves at 20°, 100° and 200°C for nickel silver CuNi18Zn27*



5 *Stress-relaxation curves at 20°, 100° and 200°C for nickel silver CuNi12Zn25*

considerably more resistant to surface oxidation and tarnishing than most other copper alloys, some designers are now using unplated nickel silvers for components which were previously made in other copper alloys and plated with precious metal to maintain low contact resistance. The extent to which this can be done, however, depends on a number of factors, such as electrical loading, mechanical loading and whether sliding contact is involved.

Aluminium-silicon-nickel piston alloys

Nickel is not normally considered to be a major alloying element in the aluminium-base alloys, but it is present in many of the cast aluminium-silicon alloys used for pistons of internal combustion engines. These alloys are divided into two broad classes, the hypoeutectic alloys containing up to 12 or 13 per cent silicon. Both types usually contain small additions of copper and magnesium—about one per cent of each is common. The nickel content normally ranges from about 0·7 to 2 per cent, although for certain high-duty hypereutectic alloys it may be as high as 3·5 per cent.

The main function of nickel in these alloys is to improve their elevated temperature properties, particularly strength and dimensional stability, without the loss in machinability which would occur if the silicon content were raised to effect the same improvements.

The precise effect of compoition on elevated temperature stength has on oly recently been elablished by Badia[4], who carried out testst at room temperature and 316°C on three standard American piston alloys after exposure to temperature for periods up to 10 000 hours. The results of this work showed that the proof-stress of the Al–9·5%, Si–3%, Cu–1% Mg alloy F132 decreased from 8·44 kg/mm² after 30 minutes at 316°C to 3·02 kg/mm² after 10 000 hours at that temperature, whereas the corresponding values for the A132 alloy (Al–12%, Si–2·5%, Ni–1%, Cu–1%Mg) were 9·28 kg/mm² and 4·29 kg/mm². Thus, after 10 000 hours' exposure to temperature, the proof stress of the nickel-containing alloy was approximately 40 per cent higher than that of the nickel-free material.

The effect of nickel on the elevated temperature properties of the aluminium-silicon alloys has been made use of by Hanafee[5], who has patented alloys containing from 4 to 9 per cent nickel with 5 to 25 per cent silicon. Until recently, alloys containing more than about 4 per cent nickel were liable to be excessively brittle. It was discovered that this brittleness was due to the presence of massive particles of nickel-aluminium compounds, and that these aluminides could be refined by restricting the iron content and correlating it with the nickel, silicon, copper and magnesium contents.

The preferred composition of alloys of this type is 10 to 16% silicon with 5 to 7% nickel. The copper and magnesium contents are again about one per cent each. Alloys of this type, although not likely to be used for normal passenger-car production, are of interest for use in high-performance and heavy-duty petrol and diesel engines.

Aluminium-nickel-manganese pressure-die-casting alloys

An alloy containing 2·5 per cent each of nickel and manganese has been recently developed in Italy, for use primarily in the burners of gas stoves. The alloy is suitable for pressure-die-casting, and this process is particularly useful for making burners with the close dimensional tolerances which are desirable when using natural gas. The flame characteristics of natural gas are such that the burner itself tends to become much hotter than is the case with coal gas; temperatures up to 560°C have been found in normal operation.

These high temperatures have given rise to several problems when normal aluminium-base die-casting alloys have been used. These alloys—normally of aluminium-silicon type—have been prone to blistering and sagging in service. In extreme cases, incipient melting has occurred. In addition, the aluminium-silicon alloys oxidize to give a dull grey finish.

The reason for blistering in the aluminium-silicon alloys is the subject of research still in progress. It is probably due to the expansion of gas pores near the metal surface, but it is not clear whether this is due to gas porosity arising from the casting process or to gas pick-up in service. Whichever is the true cause, blistering is less likely to occur if the burner material has high strength at the operating temperature. Tensile tests have shown that the aluminium-nickel-manganese alloy has higher strength at 500°C than other alloys which have been used for pressure-die-cast burners, as shown in Table VII.

TABLE VII Tensile properties of aluminium die-casting alloys at 500°C

Alloy	0·2% proof stress	Tensile strength	Elongation
	kg/mm²	kg/mm²	per cent
Al–9·5Si–1·7Cu–1·7Zn	0·32	0·8	70
Al–8Si–3·5Cu	0·33	1·0	125
Al–4Mn	1·1	1·8	23
Al–2·5Ni–2·5Mn	1·6	2·1	40

The fourth alloy listed in this table, aluminium-4% manganese, has also been used for die-cast gas burners. It also has higher strength than the aluminium-silicon type, but is somewhat susceptible to hot tearing during the die-casting process.

In order to avoid melting or sagging of the burner when exposed to high temperatures in service, it is obviously desirable to use an alloy having a high melting point. The melting characteristics of the four alloys of interest have been determined and are given in Table VIII.

TABLE VIII Melting points of aluminium die-casting alloys

Alloy	Solidus °C	Liquidus °C
Al–9·5Si–1·7Cu–1·7Zn	571	583
Al–8Si–3·5Cu	566	594
Al–4Mn	651	705
Al–2·5Ni–2·5Mn	629	680

The aluminium-nickel-manganese alloy is already in commercial production in Italy, where it was first developed, and it is being considered for use in other countries, particularly in Northern Europe, where natural gas is becoming more widely available. Consideration is also being given to its use in applications other than gas burners, since, in addition to its attractive mechanical properties, it has the ability to take and retain a good surface finish.

Conclusion

The foregoing has described some of the activity in new alloy development which is currently taking place in the field of nickel-containing non-ferrous alloys. Much of the data, including some hitherto unpublished, have been derived from work in progress in the Paul D. Merica Laboratory of International Nickel Company Inc. in the U.S.A. and the Birmingham Laboratory of International Nickel Limited in the U.K., to whom the authors are indebted for the information.

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2. Badia, F. A., Kirby, G. N. and Mihalisin, J. R.: *Trans. ASM*, **60**, (1967), pp. 395 408.
3. Worth, S. V.: *Electronic Capabilities*, Winter, 1966/67.
4. Badia, F. A.: *SAE Preprint*, No. 680267, (1968).
5. Hanafee, J. E.: U. S. Patent 3297435.

Discussions

Mr **P. Banerjee** (Indian Institute of Technology, Kharagpur) :

1. The solidus and liquidus temperatures of Al-4·5% Mn alloy are higher than those of Al-2·5 Mn-2·5 Ni alloy. What special advantage has the latter over the former regarding use of the alloys as gas-burner materials?
2. Does nickel improve the castability?

Mr **B. Weldon** (Author) :

1. Although the solidus and liquidus temperatures of the Al-2·5 Ni-2·5 Mn alloy are lower than those of the Al-4 Mn alloy, the former alloy has higher tensile properties at the orperating temperatures. For instance, the 0·2% proof stress values at 500°C are 2·52 kg/mm² and 1·73 kg/mm² respectively. At 400°C the values are 4·57 and 3·47 kg/mm² respectively. This gives the Al-2·5 Ni-2·5 Mn alloy better resistance to "sagging" during operation and confers better resistance to blistering caused by the expansion of gas porosity which is nearly always present in pressure die-castings. A further advantage is the rather better resistance of the Al-2·5 Ni-2·5 Mn alloy to tarnishing by oxidation at the operating temperatures than the Al-4 Mn alloy.
2. The addition of nickel does not in itself improve the castability and, in fact, the fluidity of the nickel-containing alloy is rather lower than that of the Al-4 Mn alloy. However, the latter material is susceptible to hot-tearing which is obviously a disadvantage in the pressure die-casting process. This has been confirmed in laboratory experiments using the Singer and Jenning Ring Test wherein a toroidal shape is cast round a steel core and materials prone to hot tearing do so under the shrinkage stresses.

   A complete account of the relative properties of these alloys is to be published soon.

Mr **M. D. Vijayavargiya,** (B. M. E. L., Hardwar) : What are the different cupro-nickel compositions used in condenser tubes of steam turbines where sea and other waters are used for cooling?

Mr **B. Weldon** (Author) : The cupro-nickels most commonly used for condenser tubes of steam turbines are those containing 10% and 30% nickel.

The 10% alloy, as specified in ASTM Bll1 and British Standard 2871, normally contains about 1·5 per cent iron and 0·8 per cent manganese. It is somewhat lower in cost than the 30% nickel alloy and has excellent resistance to corrosion by sea-water at water velocities from 0 to 4 metres/second.

The 30% nickel alloy is produced in two grades. The first, which is most common, is also covered by the above specifications and contains about 0·7% iron, 0·8% manganese. It again has excellent resistance to sea-water in the velocity range 0 to 4 metres/second but it is generally preferred over the 10% nickel alloy where the water is likely to be polluted such as in many coastal power stations. The second, rather more specialized grade, contains 2% each of iron and manganese and the higher contents of these elements confer extra resistance to abrasion/erosion by sea-water containing suspended solid matter such as sand or silt. Again, this is important in certain coastal power station installations.

These cupro-nickels can also be used in fresh waters or brackish waters (less than full strength sea-water). In the former case they are rarely used, however, since brasses such as 70/30, Admiralty brass or aluminium brass usually have sufficient corrosion resistance at a lower price.