The Choice Of Sheathing For Mineral Insulated Thermocouples H.L. Daneman, P.E.

INTRODUCTION

The mineral-insulated integrally metalsheathed (MIMS) form of thermocouple consists of matched thermocouple wires surrounded by insulating material (typically MgO) compacted by rolling, drawing or swaging until the sheath is reduced in diameter. The advantages of MIMS thermocouples are:

- Chemical isolation of wires from the surrounding atmosphere.
- Shielding of thermoelements from sources of electrical interference.
- Protection of the wires and
 insulation from domage due to ob
- insulation from damage due to shock.Flexibility of the final assembly allowing bending.

For two decades, people have credited MIMS construction with a greater capability than deserved. Quite frequently, this form has shown less stability, less durability and lower temperature limits than corresponding unsheathed elements. The nickel bearing MIMS thermocouples used above 400 °C (750 °F) are especially vulnerable to calibration instability and shortened lifetime - factors which bear heavily on thermocouple use and selection.

HYSTERESIS

Thermoelectric hysteresis is one contributor toward calibration instability. Hysteresis is a form of short-range order/disorder phenomenon occurring between 200 and 600 °C (peaking at ~ 400 °C) for Ni-Cr alloys such as Type K. It is evidenced by a calibration change of several degrees as the thermocouple temperature is cycled within this temperature band. Type N thermocouples exhibit hysteresis of up to 5°C when heated and cooled between 200 and 1000 °C (peaking around 750 °C). At 900 °C hysteresis is 2 to 3 °C. If the type K thermocouple, for example, will be used below 500 °C, hysteresis can be reduced by annealing overnight at 450 °C.

OXIDATION

Another phenomenon affecting calibration is oxidation. Ni-Cr-Al alloys (<u>e.g.</u>, Chromel*) have limited life in air above 500 °C because of oxidation. A special form of oxidation is so-called "green rot" which is preferential oxidation of Cr in atmospheres with low oxygen content (<u>e.g.</u>, sheaths in which the volume of air is limited and stagnant). Nicrosil resists oxidation up to about 1,250 °C (2,300 °F) and does not exhibit green rot.

Several new sheath materials called "Nicrobell" (**) consist of Nicrosil with 1.5% or 3.0% niobium. Nicrobell "A" is particularly formulated to be resistant to oxidation. Another new oxidation resistant sheath material called Nicrosil + (***) consists of Nicrosil plus 0.15% magnesium. It is reported (ref. 4) to exhibit less spalling and probably have a longer life than some Nicrobell version(s) tested.

Nicrosil, itself, does not have satisfactory resistance to reducing atmospheres, such as encountered in most combustion or many heat treating processes. Other adaptations of Nicrosil for use as sheath material (such as Nicrobells B, C and D) can be expected to deal with typical nonoxidizing atmospheres.

CONTAMINATION

A third influence on calibration stability is contamination. The idea behind the mineral-insulated, integrally designed, metal-sheathed thermocouple is that the uniform compression of finely divided mineral oxides (typically MgÓ) insulation surrounding the wires and filling the sheath would seal the internal volume, thereby eliminating contamination. The volume of the insulation compressed by swaging, rolling or drawing is on the order of 85% of solid material. This is useful, permitting the tubing to be bent and also permitting the manufacture of smaller diameter assemblies. It does, however, permit the intrusion of gas such as water vapor or air. It also permits vapor diffusion of elements composing the wires or sheath. Bentley and Morgan determined that the vapor-phase diffusion of Mn (manganese) through the MgO insulation has the greatest influence on thermocouple decalibration.

METAL FATIGUE

Metal fatigue is another cause of shortened thermocouple life. Differing temperature coefficients of linear expansion between sheaths and wires causes strain during heating or cooling. These strains result in eventual fracture due to metal fatigue. On heating to 900°C, the thermal expansion of Nisil differs from SS 304 by 0.4% of length. Nicrosil has only 0.05% difference in thermal expansion compared to Nisil (the leg most likely to fracture). A sheath of Nicrosil, Nicrosil ⁺ or Niobell would therefore induce less metal fatigue in either leg of the Type N thermocouple than would stainless steel.

COMPOSITION

Composition changes in SS sheathed couples are generally greater than in Inconel (****) sheathed couples. In tests performed by Anderson, *et al.*, the KN leg showed an increase in chromium but a decrease in aluminum. These changes in composition contributed the major portion of the resulting change in calibration of the thermocouple.

Most stainless steels have from 1 to 2% of manganese. Type 304 has $\approx 2\%$ manganese. Others have manganese concentrations varying from 1% to 10%. Inconel has up to 1% Mn. As a rule of thumb, each 1% of Mn in the sheath material contributes -10°C calibration shift for 1,000 hours at 1,100°C. According to Bentley, at 1,200°C, Type N in a 3 mm diameter SS sheath drifted -24°C in 1,000 hours.

HUMIDITY

There is a multiple effect of water vapor within the sheath. It is rapidly absorbed in the MgO, reducing the insulation resistance. Humidity intrusion can ruin a MIMS thermocouple assembly in as short a time as a few minutes. In lesser amounts, it destroys a protective oxide coating on Nickel-Chromium alloys, subjecting them to more rapid deterioration. The changes due to water

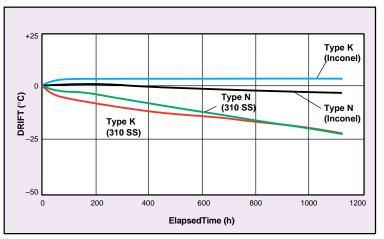


Figure 1. Drift of 3 mm diameter stainless steel sheathed and Inconel 600 sheathed type K and Nicrosil vs. Nisil thermocouples in 1200°C in vacuum. The dips in the drift curve are the result of the "in-place inhomogeneity test" where the samples were extracted from the furnace by 5 cm.

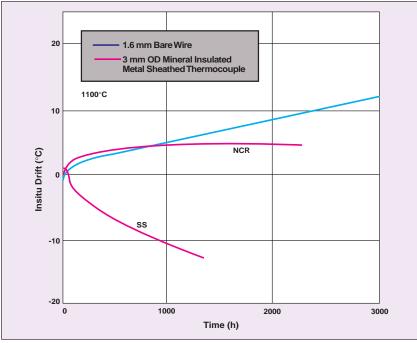


Figure 2. The insitu drift in type N thermocouples with tips held at 1100°C. Curves refer to mineral insulated metal sheathed thermocouples with 3mm OD sheaths of 310 stainless steel (SS) or Nicrosil (NCR) and 1.6mm bare wire thermocouples in air. The range in drift for the latter is also indicated.

vapor can be sufficiently severe as to make affected couples useless by reducing insulation resistance. This reduced resistance can result in misleading temperature readings, premature failure or even erroneous readings after open circuiting.

Water vapor can be introduced during thermocouple fabrication or repair, or even by changes in atmospheric pressure during air shipment or during long periods of storage (<u>e.g.</u>, six months) at construction sites. Care must be taken of hermetic seals during shipment and installation.

RECOMMENDATIONS

Although not mentioned above , there is some relationship between the diameter of these thermocouple materials and stability and longevity at elevated temperatures. The surface of the brickwork on which electrical heaters are supported becomes conductive at elevated temperatures. This leads to flow of electrical currents through thermocouple sheaths to ground, perhaps through the measuring instrument.

The temptation to use the finest sheathed thermocouples (as fine as 1 mm) should be resisted for higher temperature or corrosive industrial environments.

Stainless steel is a poorer sheath for mineral-insulated, metal-sheathed thermocouples than either Inconel 600 or modified Nicrosil when used with Ni-Cr thermocouples such as Type K or Type N. The modified Nicrosil sheathed thermocouples offer improved oxidation resistance up to 1,100 °C (1,200 to 1,250 °C for Type N), reduced failures due to differential thermal expansion, improved ductility and the elimination of the drift

problems caused by the vapor diffusion of manganese from stainless steels or Inconel.

Considering the current state of supply of the newer materials, one could well choose a low manganese (0.3% or less) Inconel sheathed Type K MIMS thermocouple until such time as modified Nicrosil sheathed Type K or N and appropriate supporting data become readily available.

- CHROMEL is a trademark of the Hoskins Manufacturing Co. NICROBELL is a trademark of NICROBELL Pty. Ltd. NICROBELL sheath alloys are patented in a number of countries including the USA
- (***) NICROSIL + is a trademark of Pyrotenax Australia Pty. Ltd.
- *) INCONEL is a trademark of the International Nickel Co.

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Material Selection Guide

This chart is a guide to selection of thermocouple sheath and thermowell materials according to process fluid. It includes factors such as catalytic reaction, contamination and electrolysis. However, there are many instances where factors other than these must be considered. It is recommended that such special applications be submitted to OMEGA ENGINEERING for recommendations.

These recommendations are only guides based on the most economical material selection. OMEGA ENGINEERING cannot be held responsible if these recommendations are not satisfactory for specific applications.

| SUBSTANCE | CONDITIONS | RECOMMENDED METAL | SUBSTANCE | CONDITIONS | RECOMMENDED METAL | SUBSTANCE | CONDITIONS | RECOMMENDED METAL |
|---------------------------------------|---|---|-------------------------------------|------------------------------------|--|--|---------------------------------|--|
| Acetate Solvents | Crude or Pure | Monel or Nickel | Ethyl Acetate | 70%5 | Monel | Picric Acid | 70°F | 304 Stainless Steel |
| Acetic Acid | 10% - 70°F 50% - 70°F | 304 Stainless Steel 304 Stainless Steel | Ethyl Chloride Ethylene Glycol | 70°F | 304 Stainless Steel Steel (C1018) | Potassium Bromide Potassium Carbonate | 70°F 1% - 70°F | 316 Stainless Steel 304 Stainless Steel |
| | 50% - 212°F | 316 Stainless Steel | Ethyl Sulphate | 70°F | Monel | Potassium Chlorate | 70°F | 304 Stainless Steel |
| | 99% - 70°F 99% - 212°F | 430 Stainless Steel 430 Stainless Steel | Ferric Chloride | 1% - 70°F 5% - 70°F | 316 Stainless Steel Tantalum | Potassium Chloride | 5% - 70°*F 5% - 212°F | 304 Stainless Steel 304 Stainless Steel |
| Acetic Anhydride | 77/0 - 212 1 | Monel | | 5% - Boiling | Tantalum | Potassium Hydroxide | | 304 Stainless Steel |
| Acetone | 212°F | 304 Stainless Steel 304, Monel, Nickel | Ferric Sulphate Ferrous Sulphate | 5% - 70°F Dilute 70°F | 304 Stainless Steel 304 Stainless Steel | | 25% - 212°F 50% - 212°F | 304 Stainless Steel 316 Stainless Steel |
| Acetylene Alcohol Ethyl | 70°F | 304 Stainless Steel | Formaldehyde | Dilute /0 F | 304 Stainless Steel | Potassium Nitrate | 5% - 70°F | 304 Stainless Steel |
| | 212°F 70°F | 304 Stainless Steel 304 Stainless Steel | Freon | 5% - 70°F | Steel (C1018) 316 Stainless Steel | Potassium | 5% - 212°F | 304 Stainless Steel |
| Alcohol Methyl | 212°F | 304 Stainless Steel | Formic Acid | 5% - 150°F | 316 Stainless Steel | Permanganate | 5% - 70°F | 304 Stainless Steel |
| Aluminum | Molten | Cast iron | Gallic Acid | 5% - 70°F 5% - 150°F | Monel | Potassium Sulphate | 5% - 70°F | 304 Stainless Steel |
| Aluminum Acetate Aluminum Sulphate | Saturated 10% - 70°F | 304 Stainless Steel 304 Stainless Steel | Gasoline | 70°F | Monel 304 Stainless Steel | Potassium Sulphide | 5% - 212°F 70°F | 304 Stainless Steel 304 Stainless Steel |
| | Saturated 70°F 10% - 212°F | 304 Stainless Steel | Glucose | 70°F 70°F | 304 Stainless Steel 304 Stainless Steel | Propane Durogallia Acid | | 304 Stainless Steel |
| | Saturated 212°F | 316 Stainless Steel 316 Stainless Steel | Glycerine Glycerol | 70 F | 304 Stainless Steel | Pyrogallic Acid Quinine Bisulphate | Dry | 304 Stainless Steel 316 Stainless Steel |
| Ammonia | All concentrations 70°F | 304 Stainless Steel | Heat Treating Hydrobromic Acid | 400/ 010°F | 446 Stainless Steel | Quinine Sulphate | Dry | 304 Stainless Steel |
| | All concentrations 212°F All concentrations 70°F | 304 Stainless Steel | Hydrochloric Acid | 48% - 212°F 1% - 70°F | Hastelloy B Hastelloy C | Resin | Molten | 304 Stainless Steel 304 Stainless Steel |
| | All concentrations 212°F | 304 Stainless Steel | · · · | 1% - 212°F | Hastelloy B | Sea Water | | Monel |
| Ammonium Sulphate | 5% - 70 F 10% - 212°F | 304 Stainless Steel 316 Stainless Steel | | 5% - 70°F 5% - 212°F | Hastelloy C Hastelloy B | Salommoniac Salicylic Acid | | Monel Nickel |
| n n | Saturated 212°F | 316 Stainless Steel | | 25% - 70°F | Hastelloy B | Shellac | 70% | 304 Stainless Steel |
| Aniline Amylacetate | All concentrations 70°F | 304 Stainless Steel Monel | Hydrocyanic Acid | 25% - 212°F | Hastelloy B 316 Stainless Steel | Soap Sodium Bicarbonate | 70°F All concentrations 70°F | 304 Stainless Steel 304 Stainless Steel |
| Asphalt | | Steel (C1018) | Hydrofluoric Acid | 20%5 | Hastelloy C | | 5% - 150°F | 304 Stainless Steel |
| | | Phosphor Bronze, Monel, Nickel | Hydrogen Peroxide | 70°F 212°F | 316 Stainless Steel 316 Stainless Steel | Sodium Bisulphate Sodium Carbonate | 5% - 70°F | Monel 304 Stainless Steel |
| Barium Carbonate | 70°F | 304 Stainless Steel | Hydrogen Sulphide | Wet and dry | 316 Stainless Steel | | 5% - 150°F | 304 Stainless Steel |
| Barium Chloride | 5% - 70°F Saturated 70°F | Monel Monel | lodine Kerosene | 70°F 70°F | Tantalum 304 Stainless Steel | Sodium Chloride | 5% - 70°F 5% - 150°F | 316 Stainless Steel 316 Stainless Steel |
| | Aqueous - Hot | 316 Stainless Steel | Lactic Acid | 5% - 70°F | 304 Stainless Steel | | Saturated - 70°F | 316 Stainless Steel |
| Barium Hydroxide Barium Sulphite | | Steel (C1018) Nichrome | | 5% - 150°F 10% - 212°F | 316 Stainless Steel Tantalum | Sodium Fluoride | Saturated - 212°F 5% - 70°F | 316 Stainless Steel Monel |
| Benzaldehyde | | Steel (C1018) | Lacquer | 70°F | 316 Stainless Steel | Sodium Hydroxide | | 304 Stainless Steel |
| Benzene Benzine | 70°F | 304 Stainless Steel Steel (C1018), | Latex Lime Sulphur | | Steel (C1018) Steel (C1018), 304, | Sodium Hypochlorite Sodium Nitrate | 5% still Fused | 316 Stainless Steel 317 Stainless Steel |
| | | Monel, Inconel | | | Monel | Sodium Peroxide | luscu | 304 Stainless Steel |
| Benzol Boracic Acid | Hot 5% Hot or Cold | 304 Stainless Steel 304 Stainless Steel | Linseed Oil Magnesium Chloride | 70°F 5% - 70°F | 304 Stainless Steel Monel | Sodium Phosphate Sodium Silicate | | Steel (C1018) Steel (C1018) |
| Bromine | 70°F | Tantalum | | 5% - 212°F | Nickel | Sodium Sulphate | 70°F | 304 Stainless Steel |
| Butadiene Butane | 70°F | Brass, 304 304 Stainless Steel | Magnesium Sulphate Malic Acid | Cold and Hot Cold and Hot | Monel 316 Stainless Steel | Sodium Sulphide Sodium Sulphite | 70°F 150°F | 316 Stainless Steel 304 Stainless Steel |
| Butylacetate | /01 | Monel | Mercury | | Steel (C1018) , 304, | Steam | 150 1 | 304 Stainless Steel |
| Butyl Alcohol Butylenes | | Copper Steel (C1018), | Methane | 70°F | Monel Steel (1020) | Stearic Acid Sulphur Dioxide | Moist Gas - 70°F | 304 Stainless Steel 316 Stainless Steel |
| | | Phosphor Bronze | Milk | 701 | 304, Nickel | | Gas - 575°F | 304 Stainless Steel |
| Butyric Acid | 5% - 70°F 5% - 150°F | 304 Stainless Steel 304 Stainless Steel | Mixed Acids (Sulphuric and Nitri | ~ | Carpenter #20 | Sulphur | Dry - Molten Wet | 304 Stainless Steel 316 Stainless Steel |
| Calcium Bisulfite | 70°F | 316 Stainless Steel | - all temp. and %) | 5 | | Sulphuric Acid | 5% - 70°F | Carp. 20, Hastelloy B |
| Calcium Chlorate | Dilute 70°F Dilute 150°F | 304 Stainless Steel 304 Stainless Steel | Molasses | | Steel (C1018), 304, Monel, Nickel | | 5% - 212°F 10% - 70°F | Carp. 20, Hastelloy B Carp. 20, Hastelloy B |
| Calcium Hydroxide | 10% - 212°F | 304 Stainless Steel | Muriatic Acid | 70°F | Tantalum | | 10% - 212°F | Carp. 20, Hastelloy B |
| | 20% - 212°F 50% - 212°F | 304 Stainless Steel 317 Stainless Steel | Nap Natural Gas | 70°F 70°F | 304 Stainless Steel 304 Stainless Steel | | 50% - 70°F 50% - 212°F | Carp. 20, Hastelloy B |
| Carbolic Acid | All 212°F | 316 Stainless Steel | Neon | 70°F | 304 Stainless Steel | | 90% - 70°F | Carp. 20, Hastelloy B Carp. 20, Hastelloy B |
| Carbon Dioxide | Dry Wet | Steel (C1018), Monel Aluminum, Monel, Nickel | Nickel Chloride Nickel Sulphate | 70°F Hot and Cold | 304 Stainless Steel 304 Stainless Steel | Tannic Acid | 90% - 212°F 70'F | Hastelloy D 304 Stainless Steel |
| | 10% - 70°F | Monel | Nitric Acid | 5% - 70°F | 304 Stainless Steel | Tar | 701 | Steel (C1018), 304, |
| Chlorex Caustic Chlorine Gas | Dry 70°F | 316SS, 317SS 317 Stainless Steel | | 20% - 70°F 50% - 70°F | 304 Stainless Steel 304 Stainless Steel | Tartaric Acid | 70°F | Monel, Nickel 304 Stainless Steel |
| | Moist 70°F | Hastelloy C | | 50% - 212°F | 304 Stainless Steel | | 150°F | 316 Stainless Steel |
| Chromic Acid | Moist 212°F 5% - 70°F | Hastelloy C 304 Stainless Steel | | 65% - 212°F Concentrated - 70°F | 316 Stainless Steel 304 Stainless Steel | Tin Tolvene | Molten | Cast Iron Aluminum, Phosphor |
| | 10% - 212°F | 316 Stainless Steel | | Concentrated - 212°F | Tantalum | | | Bronze, Monel |
| Citric Acid | 50% - 212°F 15% - 70°F | 316 Stainless Steel 304 Stainless Steel | Nitrobenzene Nitrous Acid | 70°F | 304 Stainless Steel 304 Stainless Steel | Trichloroethylene Turpentine | | Steel (C1018) 304 Stainless Steel |
| | 15% - 212°F | 316 Stainless Steel | Oleic Acid | 70°F | 316 Stainless Steel | Varnish | | 304 Stainless Steel |
| Coal Tar | Concentrated 212°F Hot | 317 Stainless Steel 304 Stainless Steel | Oleum Oxalic Acid | 70°F 5% - Hot and Cold | 316 Stainless Steel 304 Stainless Steel | Vegetable Oils | | Steel (C1018), 304, Monel |
| Coke Oven Gas | | Aluminum | | 10% - 212°F | Monel | Vinegar | | 304 Stainless Steel |
| Copper Nitrate Copper Sulphate | | 304, 316 304, 316 | Oxygen | 70°F Liquid | Steel (C1018) 304 Stainless Steel | Water | Fresh | Copper, Steel (C1018), Monel |
| Core Oils | | 316 Stainless Steel | Palmitic Acid | | 316 Stainless Steel | | Salt | Aluminum |
| Cottonseed Oil | | Steel (C1018), Monel, Nickel | Petroleum Ether Phenol | | 304 Stainless Steel | Whiskey, Wine Xylene | | 304, Nickel Copper |
| Creosols | | 304 Stainless Steel | Pentane | | 304 Stainless Steel | Zinc | Molten | Cast Iron |
| Creosote Crude | | Steel (C 1018), Monel, Nickel | Phosphoric Acid | 1% - 70°F 5% - 70°F | 304 Stainless Steel 304 Stainless Steel | Zinc Chloride Zinc Sulphate | 5% - 70°F | Monel 304 Stainless Steel |
| Cyanogen Gas | | 304 Stainless Steel | | 10% - 70°F | 316 Stainless Steel | | Saturated - 70°F | 304 Stainless Steel |
| Dowtherm Epsom Salt | Hot and Cold | Steel (C1018) 304 Stainless Steel | | 10% - 212°F 30% - 70°F | Hastelloy C Hastelloy B | | 25% - 212°F | 304 Stainless Steel |
| Ether | 70°F | 304 Stainless Steel | | | · , - | | | |