THE USE OF FE-29NI-17CO ALLOY

IN THE ELECTRONICS INDUSTRY

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Fe-29Ni-17Co alloy, also known as Kovar® alloy (a registered trademark of the Carpenter Technology Corporation), is a low expansion alloy widely utilized in the electronics industry for glass-to-metal and ceramic-to-metal sealing. The origins of this alloy can be traced to the 1930's when it was discovered that additions of cobalt lower the thermal expansivity of low expansion nickel-iron alloys. From the early uses like sealing of vacuum tubes, applications have progressed and the Fe-29Ni-17Co alloy has been applied in each new generation of electronic devices. In this paper, the metallurgy and the physical properties of the Fe-29Ni-17Co alloy are reviewed and the thermal expansivity from -175°C to 1100°C is presented. In addition, expansivity of the Fe-29Ni-17Co alloy is compared to the sealing glasses and ceramics. The desirable characteristics of the Fe-29Ni-17Co alloy, which have made it an alloy of choice in the electronics industry, are summarized.

INTRODUCTION AND HISTORY

The Fe-29Ni-17Co alloy occupies a unique position in the specialty metals industry. This alloy has made possible glass-to-metal seals and ceramic-to-metal seals capable of maintaining their integrity in a wide range of environments. The Fe-29Ni-17Co alloy has enjoyed a long history of successful use and should continue to play an important role in future electronic applications.

The early history of the alloy can be traced to researchers at the Westinghouse Research Laboratories, Pittsburgh, Pa. In 1928, P. Brace discovered that the addition of cobalt to Fe-Ni binary alloys lowers the thermal expansivity[1]. The Fe-Ni binary alloys were used to seal to the higher expansion soft glasses but could not be sealed to the lower expansion hard glasses because of the expansion mismatch. The use of hard glasses was desirable since they are less prone to cracking due to thermal shock. H. Scott, also of the Westinghouse Research Laboratories, investigated the Fe-Ni-Co alloy system in the early 1930's for use as high temperature thermostat materials. He recognized the potential of the Fe-Ni-Co alloys as metal-to-hard glass sealing alloys and succeeded in developing an alloy, namely Fe-29Ni-17Co, which matched the expansivity of borosilicate glasses, provided an excellent wettable surface for these glasses, and exhibited stability of the austentic (f.c.c.) phase over a wide range of temperatures[2]. This is essentially the same composition used today. Until that time, tungsten and molybdenum metals were exclusively used because they exhibited low thermal expansivity and could be wetted to the hard glasses. However, they are difficult to fabricate into machined parts or pin feedthroughs and are therefore expensive to manufacture and utilize in sealing applications.

The difference in thermal expansivity of the Fe-29Ni-17Co alloy as compared to the Fe-Ni binary alloys is illustrated in Figure 1. The Fe-29Ni-17Co alloy exhibits lower expansivity than either the Fe-45Ni alloy or the Fe-50.5Ni alloy, commonly known as 52 alloy (ASTM F-30). At temperatures greater than approximately 275°C, the expansivity of the Fe-29Ni-17Co alloy is lower than the Fe-36Ni alloy (Carpenter Invar "36"® alloy) and above 350°C it is lower than the Fe-40.5Ni alloy (42 alloy from ASTM F-30). The glass setting temperature of the borosilicate glasses is approximately 450°C and the Fe-29Ni-17Co alloy has been designed to match the expansion of these glasses. The Fe-Ni

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alloys exhibit much higher expansivities at this temperature.

Many early applications consisted of electrical feedthroughs for vacuum tubes. The advent of World War II created a large demand for such seals in other vacuum tube devices (e.g. magnetrons, klystrons, microwave tubes, etc.) in addition to radio tubes. This transformed the Fe-29Ni-17Co alloy from a laboratory material into a standardized product available in a variety of forms like sheet, strip, rod, and wire.

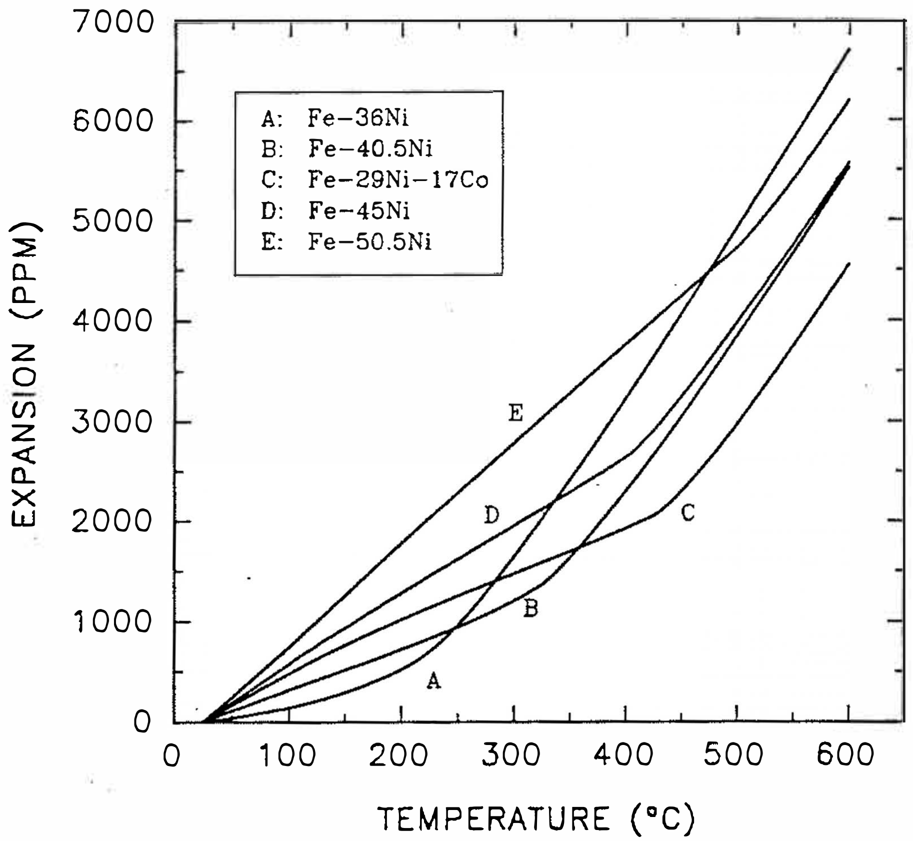

FIGURE 1. THERMAL EXPANSIVITIES OF FE-29NI-17CO ALLOY AND FE-NI ALLOYS

Ceramic-to-metal seal technology was developed in Germany prior to World War II and was refined in the United States in the early 1950's[3]. In this technology, the surface of a ceramic, like alumina, is metallized then soldered or brazed to a metal part to form a hermetic seal. The first application of this technology was for high temperature use and shock resistance to electron tubes. As the semiconductor technology developed, both the glass-to-metal and the ceramic-to-metal joining processes, which were developed by the vacuum tube industry, were used to make hermetic seals for simple transistors and semiconductors with excellent success. The subsequent electronics industry that evolved brought increased demand.

With the evolution of the integrated circuit, the Fe-29Ni-17Co alloy found use in hermetically sealing the chip within the ceramic substrate. Today, the increasing sophistication of the integrated circuit technology places even greater performance demands on component materials like the Fe-29Ni-17Co alloy. The Fe-29Ni-17Co alloy is still used for specialized vacuum tubes, mercury switches, high voltage lamps, TV video camera tubes, and similar products as well as the newer high technology electronic devices.

PRODUCTION AND FABRICATION OF FE-29NI-17CO ALLOY

The Ni-29Ni-17Co alloy is most commonly known as Kovar® alloy. It is also known as Rodar® alloy and Nicoseal® alloy. It is also referred to as F-15 alloy because of the ASTM F-15 Standard Specification which defines numerous requirements[4]. Additional tradenames have been applied by other producers of the alloy. Kovar® alloy, in wrought product form, is typically vacuum induction melted to ensure low levels of residual elements that might interfere with sealing or which might outgas in a vacuum environment. The advancement of this melting technique to commercial sized furnaces occurred in the early 1960's and significantly improved the overall quality of the alloy. The alloy is produced under a strict quality assurance program which includes inspection at various processing stages. The chemical composition is controlled within narrow limits to ensure consistent expansion properties and sealing characteristics. Processing from ingot to finished size must be done under strictest controls to provide uniform physical and mechanical properties. Procedures have been established to remove manufacturing imperfections (e.g. surface grinding and rod shaving) to ensure defect free surfaces in the finish product form. Grain size must be controlled to eliminate earring and orange peel in deep drawn parts. The Fe-29Ni-17Co alloy is produced to ASTM Standard F-15, MIL I 23011C - Class 1[5], or to the customer's own specification.

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METALLURGY OF THE FE-29NI-17CO ALLOY

The crystal structure of the Fe-29Ni-17Co alloy is face centered cubic (f.c.c.), also known as the gamma or austenitic phase. Under the influence of stress such as heavy cold working and/or subjecting the alloy to cryogenic temperatures, it can undergo transformation to body centered cubic (b.c.c.) phase also known as the alpha or martensitic phase. The presence of this phase in significant amounts is undesirable because it exhibits much higher thermal expansivity than the f.c.c. phase. If the Fe-29Ni-17Co alloy in a manufactured electronic part undergoes transformation, the instantaneous volume change can

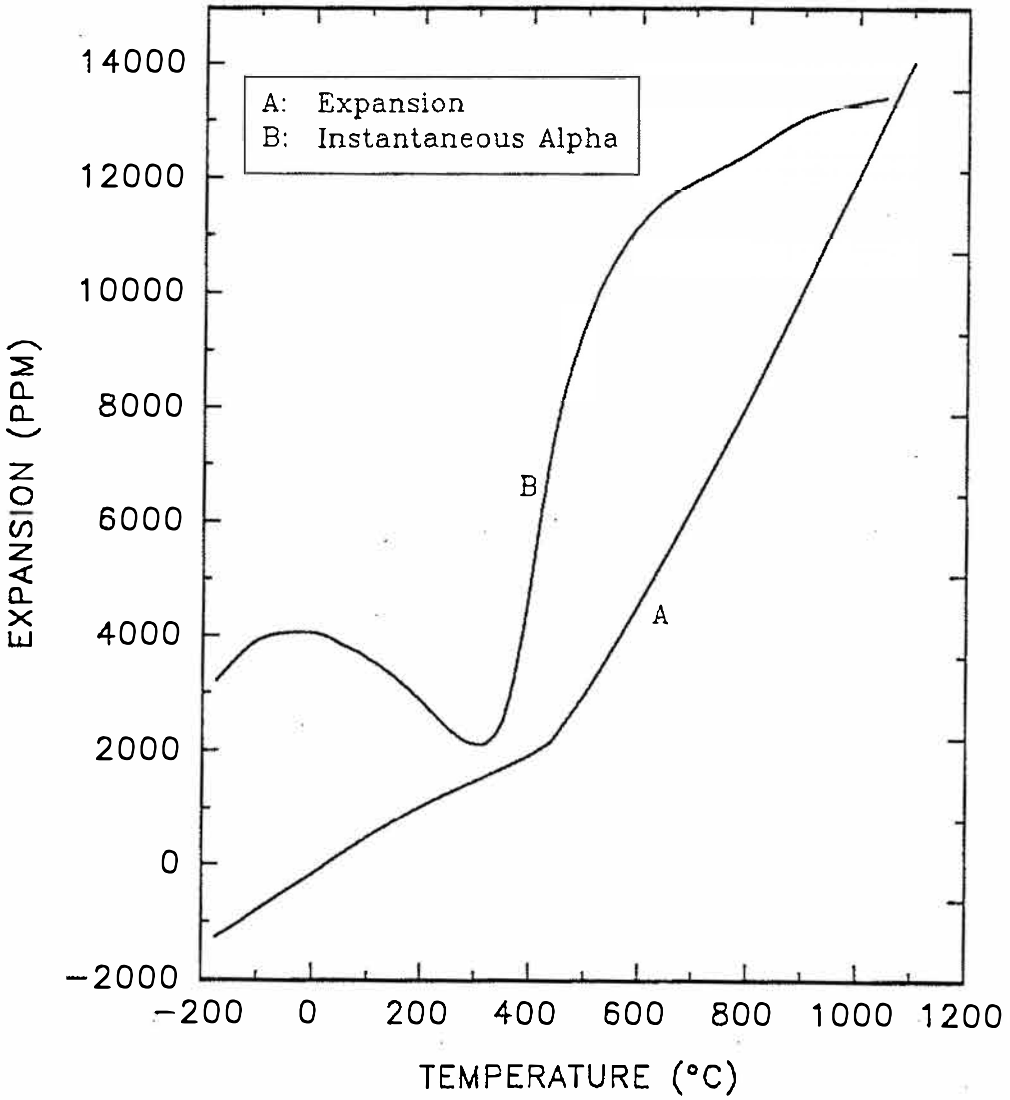

FIGURE 2. EXPANSION BEHAVIOR OF FE-29NI-17CO ALLOY

cause breakage. The standard Fe-29Ni-17Co alloy is guaranteed to have a transformation temperature below -78.5°C (dry ice-methanol temperature) and certain selected product can be supplied with capabilities lower than this temperature. Etching of the Fe-29Ni-17Co alloy to expose the grain structure can be accomplished by any number of common etchants. The specimen should be ground and polished to reveal a smooth surface suitable to examine under light microscopy. Proper handling and use of the etchants must be observed. Two etchants used are glyceregia and Marble's reagent. The compositions and precautions are documented elsewhere[6].

NATURE OF THE EXPANSION OF FE-29NI-17CO ALLOY

The unique expansion characteristic of Fe-29Ni-17Co is related to ferromagnetism. Below its Curie Temperature, the temperature below which the alloy is ferromagnetic, the alloy exhibits very low thermal expansivity. This low thermal expansivity anomaly is related to spontaneous volume magnetostriction where lattice distortion counteracts the normal lattice thermal expansivity. Above the Curie Temperature, the alloy expands at a high rate because it is no longer ferromagnetic. A number of theories have been proposed to explain the "Invar Effect" as this expansion anomaly of certain Fe-Ni alloys and Fe-Ni-Co alloys is sometimes called. Although these theories have given insight to the phenomenon, the mechanism is not yet sufficiently understood[7]. The expansion characteristics of Fe-29Ni-17Co over the temperature range of -175°C to 1100°C are shown in Figure 2. The low thermal expansivity exists from cryogenic temperatures to about 435°C, the Curie Temperature of the alloy. Also shown is the instantaneous coefficient of expansion (alpha) over this same temperature range. At temperatures below -175°C the rate of expansion will decrease and approach zero at liquid helium temperature (-269°C)[8]. The alpha averages between 4 to 6 ppm/°C from -175°C to just below the Curie Temperature where it reaches a minimum. Above the Curie temperature the Fe-29Ni-17Co alloy expands at a high rate, approximately the same rate as 300 series stainless steels. The chemistry of the Fe-29Ni-17Co alloy which was used to generate the expansion data is given in Table I and its expansion characteristics at selected temperatures are shown in Table II.

TABLE I

CHEMISTRY OF Fe-29Ni-17Co ALLOY

Ni	Co	Mn	Si	C	Al	Mg	Zr	Ti	Cu	Cr	Fe
28.96	17.37	0.24	0.11	0.014	0.002	<0.002	<0.005	0.003	0.07	0.08	bal.

The expansion measurements were conducted with a state of the art differential dilatometer in accordance with ASTM E228, "Standard Test Method for Thermal Expansion of Solid Materials witha Vitreous Silica Dilatometer". At temperatures higher than 800°C, an alumina push rod and sample holder system were used in place of the vitreous system.

TABLE II

EXPANSION CHARACTERISTICS OF FE−29NI−17CO ALLOY

TEMP (°C)	EXPANSION (ppm)	ALPHA* (ppm/°C)	C.O.E.** (ppm/°C)
−175	−1270	5.4	6.4
−150	−1130	5.9	6.5
−125	−975	6.3	6.5
−100	−810	6.4	6.5
−75	−645	6.5	6.5
−50	−485	6.5	6.5
−25	−330	6.6	6.6
0	−175	6.6	6.9
25	0	6.6	−−
50	165	6.3	6.5
100	480	5.9	6.4
150	765	5.3	6.1
200	1025	4.9	5.8
250	1260	4.5	5.6
300	1475	4.3	5.4
350	1695	4.4	5.2
400	1925	5.2	5.1
435	2130	9.3	5.2
450	2300	11.9	5.4
500	2975	14.6	6.3
550	3740	15.8	7.1
600	4555	16.7	7.9
650	5400	17.3	8.6
700	6275	17.8	9.3
750	7175	18.1	9.9
800	8090	18.5	10.4
850	9060	19.0	11.0
900	10045	19.3	11.5
950	11050	19.5	11.9
1000	12030	19.7	12.3
1050	13015	19.8	12.7
1100	14030	20.0	13.1

* Instantaneous Alpha (Instantaneous Coefficients of Expansion)
**Average Coefficients of Expansion Determined from 25°C

Figure 3 compares the thermal expansivity of borosilicate glass to the Fe-29Ni-17Co alloy. There is a close match of the Fe-29Ni-17Co alloy to the glass setting temperature of borosilicate glass which is approximately 450°C. This provides for essentially stress free glass-to-metal seals which was the original design feature of the alloy. Figure 4 compares the expansivities of alumina, beryllia, and the Fe-29Ni-17Co alloy. These ceramic materials are most commonly used to seal to the Fe-29Ni-17Co alloy from soldering temperatures of approximately 250°C to brazing temperatures of 1100°C, depending on the application. Although there is expansion mismatch of the Fe-29Ni-27Co alloy to either alumina or beryllia, good hermetic seals can be made using these materials when the proper precautions are undertaken in the design of the seal. For example, compression joints are preferable so the higher expansivity component should be placed on the outside whenever possible. A sufficient amount of clearance between

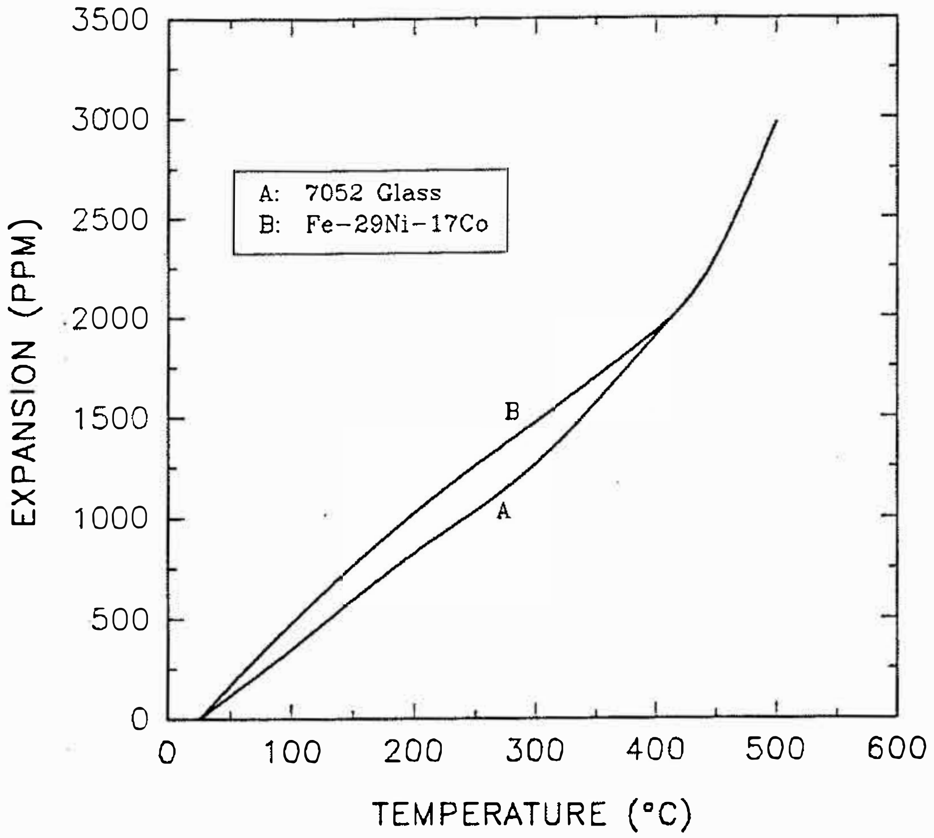

FIGURE 3. THERMAL EXPANSIVITIES OF FE-29NI-17CO ALLOY AND 7052 BOROSILICATE GLASS

the ceramic component and Fe-29Ni-17Co alloy component must be taken into consideration to allow proper brazing. In some applications, like low temperature soldering of large parts, the Fe-45Ni alloy is used to seal to alumina and beryllia, as it provides a closer expansion match.

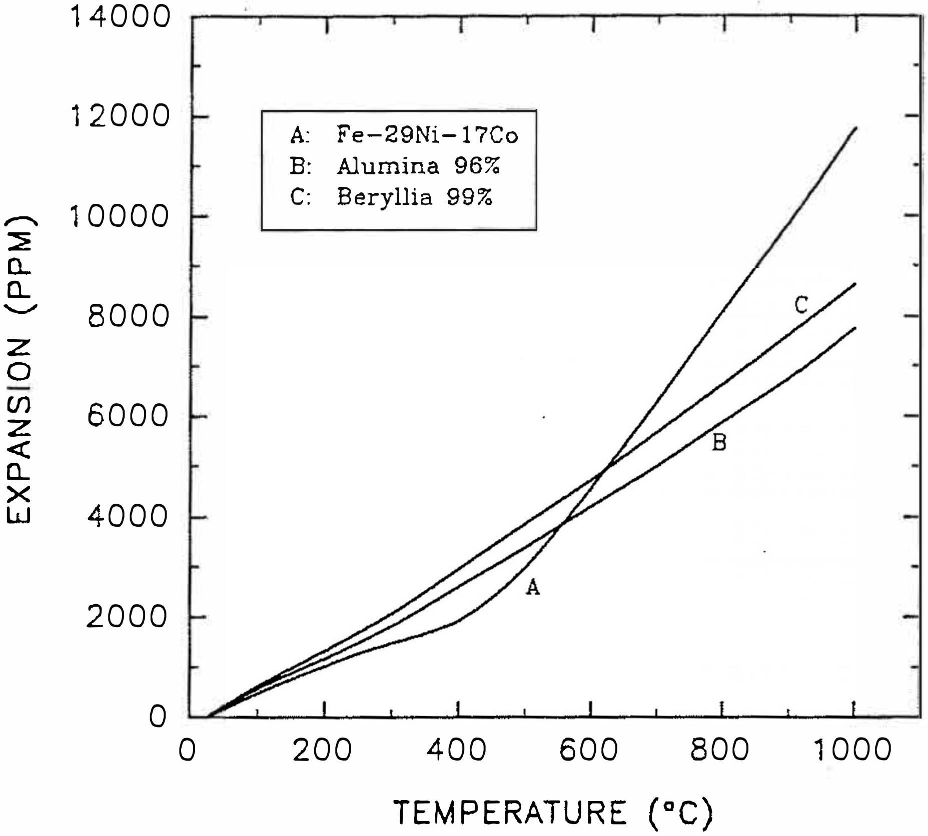

FIGURE 4. THERMAL EXPANSIVITIES OF FE-29NI-17CO ALLOY, AND ALUMINA AND BERYLLIA CERAMICS

GENERAL PHYSICAL PROPERTIES

Table III lists some of the general physical properties of the Fe-29Ni-17Co alloy.

TABLE III	
PHYSICAL PROPERTIES OF Fe-29Ni-17Co ALLOY	
Specific Gravity	8.36
Thermal Conductivity	17 W/m-°C (10 BTU/hr-ft-°F)
Electrical Resistivity	49 micro-ohm-cm (294 ohm-cir mil/ft)
Curie Temperature	435°C (815°F)
Specific Heat	0.11 cal/g-°C (0.11 BTU/lb-°F)
Melting Point	1450°C (2640°F)

The coefficients of thermal expansion of the Fe-29Ni-17Co alloy are compared to other component materials in Table IV. The alloy is compatible to the other materials, excepting copper, indicating that at temperatures up to 300°C thermal stresses among these components are minimized.

TABLE IV

COEFFICIENTS OF EXPANSION OF SELECTED MATERIALS (25°C–300°C)

Copper	17 ppm/°C	9.8 ppm/°F
Molybdenum	5.2	2.9
Tungsten	4.5	2.5
Fe–29Ni–17Co	5.4	3.0
Alumina	6.6	3.7
Beryllia	7.5	4.2
Silicon Carbide	4.9	2.7
Aluminum Nitride	4.5	2.5
Silicon	4.1	2.3

The Fe-29Ni-17Co alloy exhibits relatively low thermal conductivity and specific heat. Many applications require careful attention to the overall thermal management of the electronic device. For example, in an integrated chip device the heat must not be allowed to build up because increased temperatures degrade performance and lower the life expectancy[9]. A comparison of thermal conductivities of selected electronic component materials is shown in Table V. The thermal conductivity of Fe-29Ni-17Co alloy approaches that of alumina, but both of the these materials are much lower than other component materials.

TABLE V

THERMAL CONDUCTIVITIES OF SELECTED MATERIALS (25°C)

Copper	400 W/m–°C	230 BTU/h–ft–°F
Molybdenum	147	84
Tungsten	166	96
Fe–29Ni–17Co	17	10
Alumina (96%)	21	12
Beryllia (99%)	230	132
Silicon Carbide	81	47
Aluminum Nitride	250	145
Silicon	150	87

The Fe-29Ni-17Co alloy is ductile and can readily be deep drawn to shaped parts and/or stamped to exacting dimensions. It can be machined at low speeds with high speed steel or tungsten carbide tools with proper lubrication. The Fe-29Ni-17Co alloy machines similarly to Monel® alloy R-405. It can be purchased in several tempers, including full annealed, deep draw quality, and hard (i.e. cold rolled or cold drawn). Typical mechanical properties are shown in Table VI.

TABLE VI

MECHANICAL PROPERTIES OF FE−29NI−17CO ALLOY (as annealed)

Tensile Strength	75 ksi (517 MPa)
Yield Strength	50 ksi (345 MPa)
Elongation in 2 inches	30%
Hardness, Rockwell	HRB 80
Elastic Modulus	20 Mpsi (138 MPa)
Shear Modulus	7.5 Mpsi (52 MPa)
Poisson's Ratio	0.32

The Fe-29Ni-17Co alloy is not considered corrosion resistant and will "rust" in relatively mild industrial environments. Due to its nickel content, it will exhibit more resistance to "rusting" than iron. When exposed to 95% humidity at 35°C, the alloy will show signs of rust within 200 hours[10].

GENERAL PROCEDURES FOR USE

For glass-to-metal and ceramic-to-metal sealing, and metal-to-metal joining, specific manufacturing procedures are implemented depending on the product being made and the manufacturing resources being utilized. Generally, for glass-to-metal sealing the following steps should be included:

1. Cleaning the Fe-29Ni-17Co alloy part.
2. Decarburization (if necessary).
3. Oxidation (to provide a wettable surface for the glass).
4. Application of the glass.
5. Annealing to relieve thermal stresses.

The Fe-29Ni-17Co parts must be cleaned by degreasing

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and acid etching to remove residual compounds from fabrication. Decarburization is used to reduce the carbon level at the surface and remove surface contaminants. Some applications may not need the decarburization treatment if the parts have been thoroughly cleaned and the Fe-29Ni-17Co alloy is known to be from a low carbon lot of material. This can only be verified by sealing trial parts without the decarburization step. A typical decarburization treatment consists of exposure to 900°C-1050°C in a wet hydrogen, or dissociated ammonia, atmosphere with a dew point of approximately 20°C. Oxidation of the Fe-29Ni-17Co parts to provide a uniform oxide (wettable to a glass surface) occurs in the temperature range 700°C-900°C in dry air. Other oxidizing atmospheres and temperatures are also used[11]. The thickness of the oxide layer is critical. If the layer is too thick, scaling or flaking can occur preventing a good seal to the glass. If the layer is too thin, the part will not wet to the glass sufficiently. Control of the process can be monitored by measuring weight gain on a standard sample. Sealing to borosilicate glass usually is at approximately 1050°C in a slightly oxidizing atmosphere. After sealing, the part may be stress relieved at a temperature of 600°C followed by a slow cool to room temperature.

For metal-to-ceramic sealing the following steps generally should be included:

1. Metallization of the ceramic surfaces to be sealed.
2. Cleaning of the Fe-29Ni-17Co alloy part.
3. Plating of the Fe-29Ni-17Co alloy part with Ni and/or Cu.
4. Soldering or brazing of the metallized ceramic to the Fe-29Ni-17Co part.

The ceramic part must be metallized in order to provide a wettable surface suitable for soldering or brazing to the Fe-29Ni-17Co alloy. This frequently consists of the "moly-manganese" technique where a thin layer of paint solids containing molybdenum, manganese, and other metals in oxide form are fired at elevated temperature resulting in a dense refractory metal layer bonded to the surface of the ceramic. The Fe-29Ni-17Co parts must be cleaned by degreasing and acid etching to remove any residual surface contaminants. The Fe-29Ni-17Co alloy is often plated with nickel to facilitate wettability by the solder or brazing alloy. It sometimes is plated with copper or gold. The use of solders is restricted to applications where the high vapor pressure of the solder constituents do not interfere with the device integrity. Copper, copper-gold, and copper-silver alloys are generally used for brazing in this order of preference. Silver can cause intergranular cracking in the Fe-29Ni-17Co alloy and the brazing surface should be plated with nickel or copper to retard penetration of the silver. The proper design of joints and fixturing is critical for brazed parts. The brazing operation is carried out in a reducing atmosphere at temperatures in the range of 800°C-1100°C.

SUMMARY

The Fe-29Ni-17Co alloy has been used in the electronics industry for over 60 years. The initial intention was to provide a lower cost metal to seal to the "hard" borosilicate glasses. These metal-to-glass seals are essentially stress-free because there is little expansion mismatch between the Fe-29Ni-17Co alloy and borosilicate glasses. In addition, this alloy forms an oxide which is readily wetted by these glasses, which provides high quality seals of good strength and hermeticity. The technology was then developed for metal-to-ceramic sealing using the Fe-29Ni-17Co alloy as leadthroughs and seals for ceramic vacuum tubes. This technology base was eventually transferred to the making of transistors and semiconductors. As the solid state industry developed, the use of the Fe-29Ni-17Co alloy was extended to integrated circuitry for leadthroughs and to provide environmental protection. The favorable characteristic of the Fe-29Ni-17Co alloy is ease of fabrication because the alloy is ductile and can be stamped and deep drawn into parts on a mass production scale. By virtue of its low thermal expansivity (due to the "Invar Effect"), it is compatible to many of the component materials used in the electronics industry. The alloy can be soft soldered, brazed, or welded to itself, certain ceramics and other metals which allows for a variety of production methods to manufacture electronic parts. The versatility of Fe-29Ni-17Co can make it cost effective in many diverse electronic device applications.

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