LOW THERMAL EXPANSION ALLOYS AND COMPOSITES

Edited by

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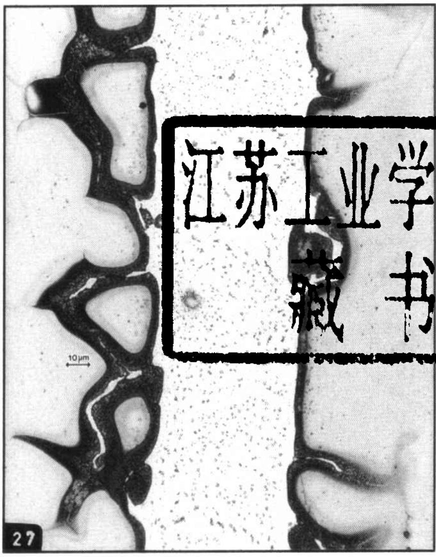

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Microstructure of a high Si + Cr heat of Fe-29Ni-17Co (Kovar™) Alloy showing intergranular penetration of liquid copper following brazing in a wet hydrogen atmosphere (from the paper by G.E. Crabtree and G.W. Franti)

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PREFACE

This conference proceedings volume documents, in archival form, selected presentations which were made at the committee-sponsored symposium, "Low Thermal Expansion Alloys and Composites" which was held as part of the Fall Meeting of TMS held at Chicago, Illinois from November 2 to 5, 1992. The symposium was co-sponsored by the Refractory Metals Committee of the Structural Materials Division (SMD) and the Electronic Packaging and Interconnection Materials Committee of the Electronic, Magnetic and Photonics Materials Division (EMPMD). The symposium was organized with the intention of presenting a survey of the processing and properties of low thermal expansion alloys and composites for electronic applications. Three sessions were held, with the first session concentrating on low thermal expansion composites, and the latter two sessions focusing on low and controlled thermal expansion alloys.

The organization of this volume reflects the fact that a majority of the papers which were submitted for the conference dealt with the controlled expansion alloy Fe-29Ni-17Co – better known to the world as "Kovar™"*. This was in part the intent of the organizers, due to widespread use of this alloy for controlled expansion applications. A survey by the editors found no single volume that focuses on recent technical information for controlled expansion alloys. This is especially important for the Fe-29Ni-17Co alloy since it was originally designed as a glass-to-metal sealing alloy, but has also found widespread application in soldered electronic circuitry and metal/ceramic brazed components for vacuum-electronic applications. It should also be noted that there are three common-domain specifications for the Fe-29Ni-17Co alloy, depending upon application: the ASTM F15 and MIL-I-23011C (Class 1 alloy) specifications are intended for glass-to-metal sealing applications, and are also appropriate for soldered electronic applications; while the recently published ASTM F1466 specification is intended for metal/ceramic brazing applications and incorporates more stringent chemistry requirements than the other two specifications. Selected papers in the first section of this book, especially the two papers co-authored by G.E. Crabtree and G.W. Franti, as well as the paper by G.C. Nelson and R.W. Buttry, discuss the tendency of trace oxide formers to segregate to the surface of this alloy, along with the need for the ASTM F1466 specification. The paper by L.L. Harner is an excellent overview of the electronic applications of the Fe-29Ni-17Co alloy.

The other papers on Fe-29Ni-17Co alloy focus on processes and properties resulting from brazing or other joining processes. The paper by J.J. Stephens and P.F. Hlava examines the effect of time and temperature on alloying of metal/ceramic Cu brazes for electronic applications. The following two papers deal with properties of brazed lead wires: J.J. Stephens F.A. Greulich and L.C. Beavis discuss grain growth, while K.S. Dogra discusses fatigue properties of Fe-29Ni-17Co alloy lead wires. The behavior of Kovar™ when it is welded is described in the papers by C.V. Robino C.R. Hills and P.F. Hlava, and P.M. Mizik. Finally, the solderability of Kovar™ is detailed in the paper by P.T. Vianco and F.M. Hosking.

The second section of this volume describes the properties and behavior of low thermal expansion composites. Composites are finding increased use in low thermal expansion applications due to the ability to tailor the expansion behavior of the alloy. The papers presented on low thermal expansion composites are indicative of the variety of the materials and uses of composites. Y.C. Chen and G.S. Daehn describe the creep properties of Al-40%Si composites. The use of $Al\text{-}Al_2O_3$ composites for heat sinks is discussed in the paper by M.C. Breslin, G.S. Daehn and H.L. Fraser. The ability to maintain dimensional stability in whisker reinforced 6061 Al is described in the paper by M.J. Davidson, K.K. Hamann and R. Arrowood. Finally, the thermomechanical behavior of the Al-AlN composite is described by S.W. Lai and D.D.L. Chung.

The editors would like to extend their sincere appreciation to the authors of the papers in this volume for their efforts in preparing excellent manuscripts that describe the current state of knowledge of low thermal expansion materials. We would also like to thank TMS for their assistance in publishing this volume and specifically Janet Urbas at TMS who acted as our liaison in the details of the publishing process.

John J. Stephens

Darrel. R. Frear

* *Note: Kovar™ is a registered trademark of Carpenter Technology Corporation.*

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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 favorable characteristics of the Fe-29Ni-17Co alloy, which have made it an alloy of choice in the electronics industry, are summarized.

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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.

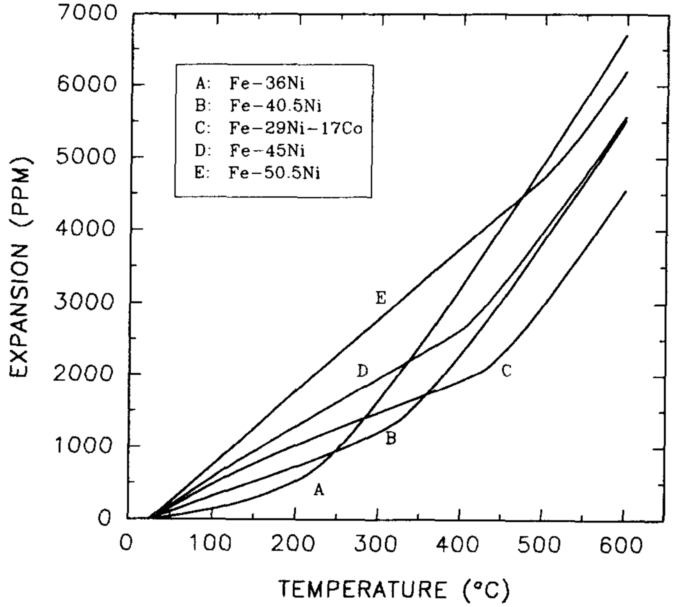

FIGURE 1. THERMAL EXPANSIVITIES OF FE-29NI-17CO ALLOY AND FE-NI ALLOYS

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

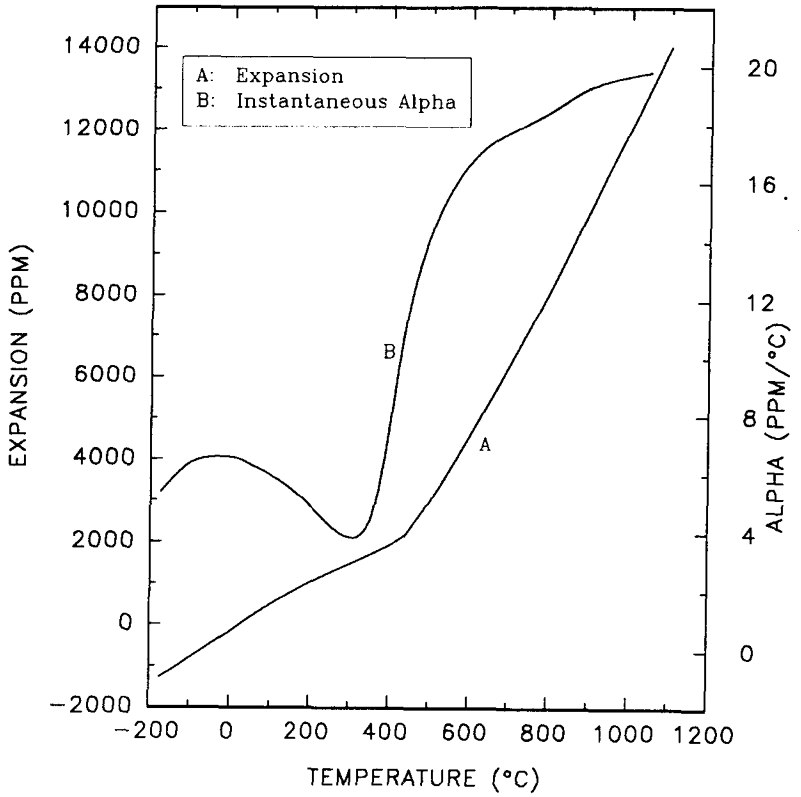

FIGURE 2. EXPANSION BEHAVIOR OF FE-29NI-17CO ALLOY

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

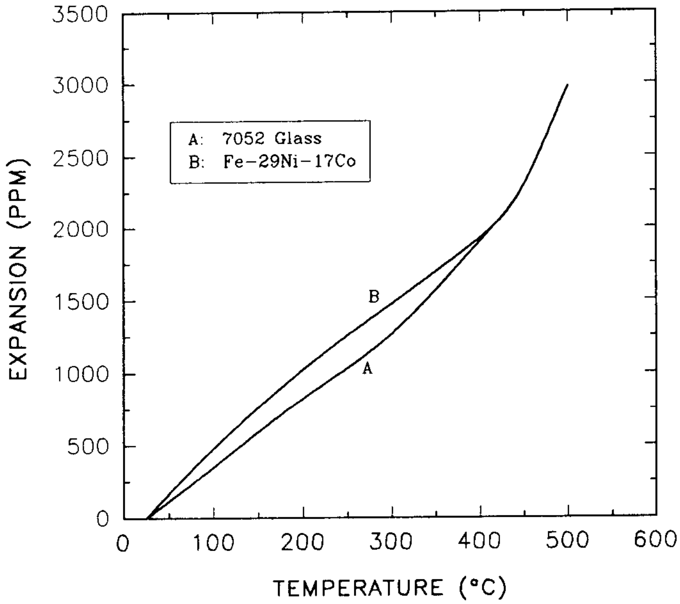

FIGURE 3. THERMAL EXPANSIVITIES OF FE-29NI-17CO ALLOY AND 7052 BOROSILICATE GLASS

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

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