

Nov. 8, 1966

F. ZIMMER
COMPOSITE STRUCTURES MADE BY BONDING
CERAMICS, CERMETS, ALLOYS, HEAVY
ALLOYS AND METALS OF DIFFERENT
THERMAL EXPANSION COEFFICIENT

3,284,174

Filed April 16, 1962

3 Sheets-Sheet 1

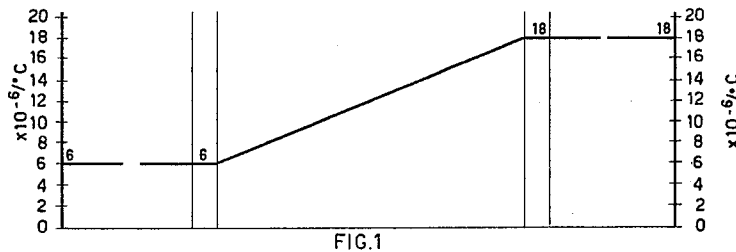


FIG. 1



FIG. 2

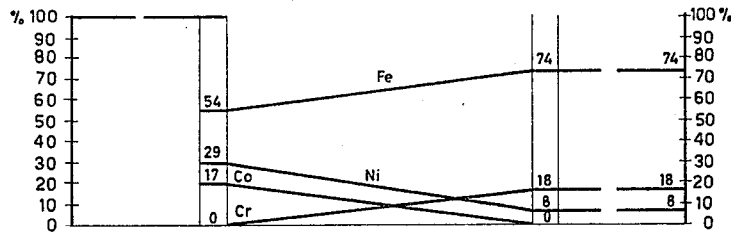


FIG. 3

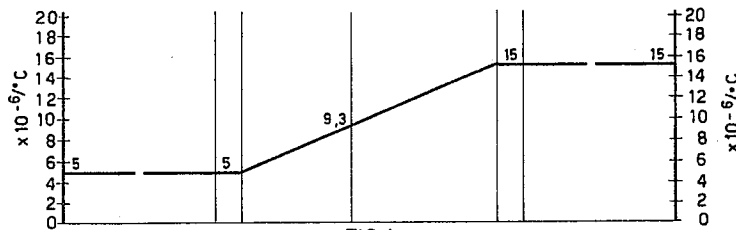


FIG. 4

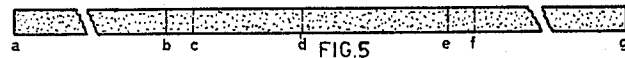


FIG. 5



FIG. 6

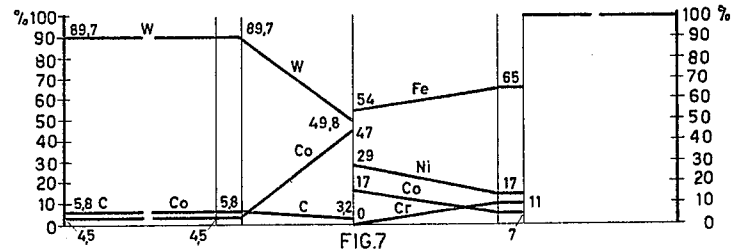


FIG. 7

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3 Sheets-Sheet 2

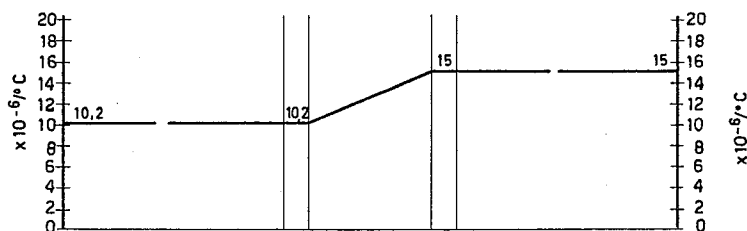


FIG. 8



FIG. 9

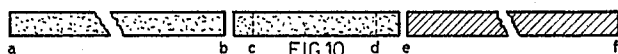


FIG. 10

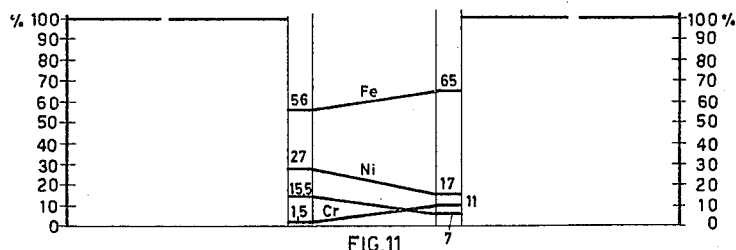


FIG. 11

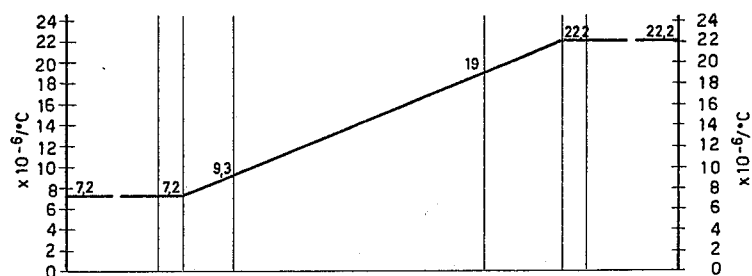


FIG. 12

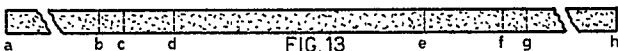


FIG. 13



FIG. 14

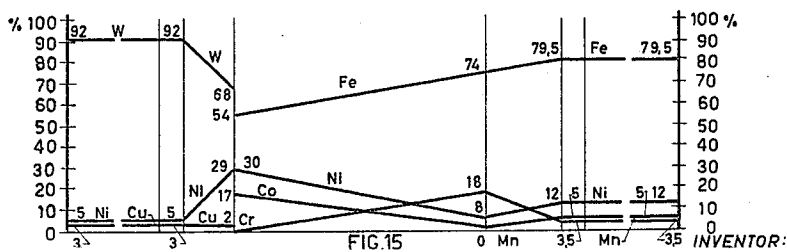


FIG. 15

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3 Sheets-Sheet 3

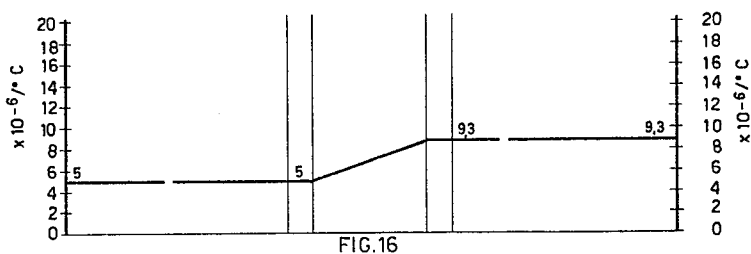


FIG. 16

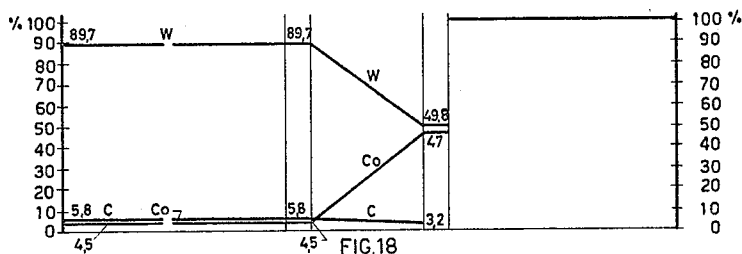


FIG. 18

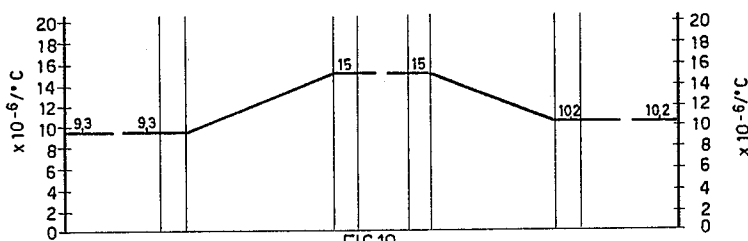


FIG.19

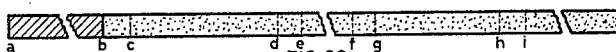


FIG. 20

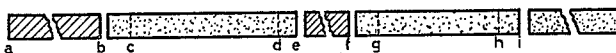


FIG. 21

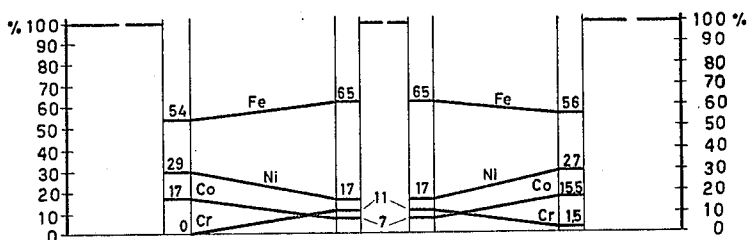


FIG.22

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COMPOSITE STRUCTURES MADE BY BONDING CERAMICS, CERMETS, ALLOYS, HEAVY ALLOYS AND METALS OF DIFFERENT THERMAL EXPANSION COEFFICIENT

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14 Claims. (Cl. 29—183.5)

This invention relates to improvements in the methods of making assemblies by bonding ceramics, cermets, alloys, heavy alloys and metals of different thermal expansion coefficients.

The assemblies may be made by bonding components of ceramics, cermets, alloys, heavy alloys and metals of different thermal expansion coefficients by means of one or more connecting parts, the components being made by powder metallurgy or by conventional methods and the connecting part for each pair of components being made by powder metallurgy and having an expansion coefficient increasing, not in a stepwise fashion but in a continuously progressive manner from that of one component to that of the other component, the said connecting part being characterized by a variable composition which is that of one or several alloy systems chosen in the following systems:

Expansion coefficient $\times 10^{-6}/^{\circ}\text{C.}$;
range of temperature,
20 $^{\circ}\text{C.}$ —700 $^{\circ}\text{C.}$

(1) 54% Fe, 29% Ni, 17% Co, 0% Cr, to 74% Fe, 18% Cr, 8% Ni, 0% Co	9.3—19
(2) 58% Fe, 42% Ni, 0% Cr, to 74% Fe, 18% Cr, 8% Ni	10—19
(3) 100% Zr, 0% Ti, to 0% Zr, 100% Ti	6.5—10
(4) 94% W, 6% C, 0% Co to 0% W, 0% C, 100% Co	4.5—14.4
(5) 81.5% Ti, 18.5% C, 0% Ni to 0% Ti, 0% C, 100% Ni	8—15.4
(6) 92% W, 5% Ni, 3% Cu to 0% W, 100% Ni, 0% Cu	7.2—15.4
(7) 74% Fe, 18% Cr, 8% Ni, 0% Mn to 79.5% Fe, 12% Ni, 5% Mn, 3.5% Cr	19—22.2

Under the expression "bonding" it is understood any of the various joining techniques which assure that atoms of the pieces to be joined are brought close enough together to allow their interatomic attraction forces to become effective.

Such joining techniques are for example:

Ultrasonic welding;
Cold pressure welding;
Hot pressure welding;
Solid-to-solid sintering, for example by powder metallurgy;
Liquid-to-solid bonding, for example, high temperature brazing;
Fusion welding without a filler metal, for example flash welding;
Fusion welding with a filler metal, for example arc welding;
Bonding of ceramic to metal, for example by the Mo-Mn process.

The bonding of two materials having different expansion coefficients is usually difficult to carry out. From the point of view of the degree of difficulties which can be met we can distinguish three typical cases, to start with the most severe one:

FIRST CASE

In this case, the difference between the expansion coefficients of the two materials is such that it prevents the completion of the joint. The critical value of this differ-

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ence depends closely on the ductility or the brittleness of the two materials to be bonded.

When the two materials are ductile, for example two metals, the critical value of the difference is quite large: of the order of 6 to $8 \times 10^{-6}/^{\circ}\text{C.}$

When this value is reached or exceeded, the joint is, during cooling from the welding or brazing temperature, the seat of very severe thermal stresses which can easily produce a spontaneous fracture of the joint before or after cooling to room temperature.

For example, the welded joint between "Kovar" (54% Fe, 29% Ni, 17% Co) and austenitic steel with expansion coefficients of respectively 9.3 and $19 \times 10^{-6}/^{\circ}\text{C.}$ is prone to spontaneous cracking.

The most difficult case is met when one material is brittle or both. In such a case, the critical difference between the expansion coefficients may be lower than $1 \times 10^{-6}/^{\circ}\text{C.}$

That is the case when ceramics are to be bonded to metals. In such a condition, the expansion coefficients must be matched closely to prevent rupture.

SECOND CASE

This case is less difficult to handle but not without eventual drawbacks. It can be illustrated by the welding of two ductile metals having slight differences between their expansion coefficients: 4 to $5 \times 10^{-6}/^{\circ}\text{C.}$ —for example a joint between ferritic steel ($15 \times 10^{-6}/^{\circ}\text{C.}$) and austenitic steel ($19 \times 10^{-6}/^{\circ}\text{C.}$).

Such a joint is not difficult to be made, but when the weld is periodically heated and cooled, it is subject to repeated thermal stresses which produce microcracks with consequent complete failure of the welded joint.

THIRD CASE

This case, presenting no special difficulties and no risk of drawbacks, is illustrated by the welding of two metals or alloys having a good mutual weldability and expansion coefficients which differ slightly (difference 1 to $2 \times 10^{-6}/^{\circ}\text{C.}$). In such a situation, the joint can stand the thermal stresses during cooling after welding and during thermal cycling.

It has previously been proposed by the present applicants in patent applications Nos. 722,582 and 819,290, now Patents Nos. 3,052,016 and 3,123,447, respectively, to produce a joint between two materials whose coefficients of expansion do not match.

In patent application No. 722,582 the two materials to be joined are ferritic steel and austenitic steel. In patent application No. 819,290 the two materials are chosen in a group consisting of metals with high melting point, cermets, hard intermetallic compounds, stainless steels, refractory alloys, austenitic steels.

According to the said patent application No. 819,290 the joint between two materials whose differences in thermal expansion is higher than 2×10^{-6} , is effected by means of a connecting piece inserted between the two materials and joined to the two materials at its two ends, the said connecting piece being made by powder metallurgy and having an expansion coefficient increasing, not in a stepwise fashion, but in a continuously progressive manner from that of one material to that of the second material, and is characterized by the presence of the connecting piece of an iron-nickel alloy of a continuously variable composition, with or without addition of chromium and cobalt.

In the same patent application it is claimed that the transition portion of the connecting piece may consist of two or several alloy systems.

The alloy systems mentioned in the said application are:

- (1) From 53% Fe, 30% Ni, 17% Co, 0% Cr to 74% Fe, 18% Cr, 8% Ni, 0% Co;
- (2) From 58% Fe, 42% Ni, 0% Cr to 74% Fe, 18% Cr, 8% Ni;
- (3) From 100% Zr, 0% Ti to 0% Zr, 100% Ti.

The said alloy systems allow of obtaining all intermediary expansion coefficients between the extreme values of:

	Range of temperature from 20° C. to 500° C.	Range of temperature from 20° C. to 800° C.
1.-----	From 6.4×10^{-6} to 18×10^{-6}	From 9.3×10^{-6} to 19×10^{-6}
2.-----	From 7.6×10^{-6} to 18×10^{-6}	From 10×10^{-6} to 19×10^{-6}
3.-----	From 6.4×10^{-6} to 9.7×10^{-6}	From 6.5×10^{-6} to 10×10^{-6}

I disclaim any combination covered by the present application which is already covered by the said prior patent application No. 819,290 and prior patent application No. 722,582.

The object of the present invention is to add to these three alloy systems other alloy systems with a view to extending the extreme values of the thermal expansion coefficients and to make in this way possible assemblies by bonding components of ceramics, cermetes, heavy alloys of very low expansion coefficients and also their bonding to metals with even higher thermal expansion coefficients.

The alloy systems and the extreme values of their thermal expansion are as follows:

- (1) From 54% Fe, 29% Ni, 17% Co, 0% Cr to 74% Fe, 18% Cr, 8% Ni, 0% Co
(20–500° C.) 6×10^{-6} to 18×10^{-6}
(20–600° C.) 7.9×10^{-6} to 18.5×10^{-6}
(20–700° C.) 9.3×10^{-6} to 19×10^{-6}
- (2) From 58% Fe, 42% Ni, 0% Cr to 74% Fe, 18% Cr, 8% Ni
(20–500° C.) 7.6×10^{-6} to 18×10^{-6}
(20–600° C.) 8.7×10^{-6} to 18.5×10^{-6}
(20–700° C.) 10×10^{-6} to 19×10^{-6}
- (3) From 100% Zr, 0% Ti to 0% Zr, 100% Ti
(20–500° C.) 6.4×10^{-6} to 9.7×10^{-6}
(20–600° C.) 6.45×10^{-6} to 9.9×10^{-6}
(20–700° C.) 6.5×10^{-6} to 10×10^{-6}
- (4) From 94% W, 6% C, 0% Co to 0% W, 0% C, 100% Co
(20–700° C.) 4.5×10^{-6} to 14.4×10^{-6}
- (5) From 81.5% Ti, 18.5% C, 0% Ni to 0% Ti, 0% C, 100% Ni
(20–700° C.) 8×10^{-6} to 15.4×10^{-6}
- (6) From 92% W, 5% Ni, 3% Cu to 0% W, 100% Ni, 0% Cu
(20–700° C.) 7.2×10^{-6} to 15.4×10^{-6}
- (7) From 74% Fe, 18% Cr, 8% Ni, 0% Mn to 79.5% Fe, 12% Ni, 5% Mn, 3.5% Cr
(20–700° C.) 19×10^{-6} to 22.2×10^{-6}

The possible combinations of the above seven basic alloy systems allow of obtaining all intermediary thermal expansion coefficients between the extreme values of 4.5×10^{-6} and 22.2×10^{-6} , and therefore allow of matching very closely the expansion coefficients of materials of low, medium and high expansion coefficients, for example:

Materials of low coefficients of expansion: 4.10^{-6} to 10×10^{-6} ;

Ceramics, cermetes, heavy alloys, hard intermetallic compounds;

Tungsten, molybdenum, zirconium, titanium;

Materials of medium coefficients of expansion 10.10^{-6} to 16×10^{-6} ;

Stainless steels with 12% Cr, ferritic steels, nickel based and cobalt based superalloys, cobalt and nickel;

Materials of high coefficients of expansion: 16.10^{-6} to 22×10^{-6} ;

Beryllium, austenitic steels, copper, aluminum.

Other characteristic features of the invention will appear from the following examples of bonding dissimilar materials having different thermal expansion coefficients.

Assemblies of ceramics with metals or alloys

The ceramics, widely used in electrotechnique, for nuclear energy applications and for ceramic cutting tools, are for example: soft and hard glasses, alumina, zirconia, steatite, forsterite, whitewares.

The bonding of ceramics to metals is usually complicated by large differences in thermal coefficients of expansion and by the brittleness of ceramics.

As above stated, when ductile metals are welded together it is possible to realize a weld even if the difference in thermal coefficients of expansion is of the order of 4.10^{-6} to 6×10^{-6} .

In the case of glass, owing to its great brittleness, the difference in expansion coefficients between glass and metal must not exceed 1×10^{-6} and the expansion curve of the glass and the metal must match closely below the softening temperature of the glass, since substantial differences at intermediate temperatures cause the glass to crack and to separate from the metal.

For this reason, a specific glass can be bonded only to a special alloy whose thermal expansion coefficients closely match that of the glass. For example, soft glasses with an expansion coefficient of 11×10^{-6} (20–500° C.) are bonded or sealed with special alloys matching this coefficient of expansion, for example:

Chromium-iron-alloy: 28% Cr, 72% Fe: (20° C.–500° C.): 11×10^{-6} .

Alloy 42% Ni, 52% Fe, 6% Cr: (20° C.–500° C.): 10.8×10^{-6} .

The hard glasses which have a low expansion coefficient of 4×10^{-6} to 6×10^{-6} (20° C.–500° C.) are bonded usually to low expansion metals or alloys, such as:

Tungsten (20° C.–500° C.): 4.6×10^{-6} .

Molybdenum (20° C.–500° C.): 5.5×10^{-6} .

"Kovar" (29% Ni, 17% Co, 54% Fe) (20° C.–500° C.): 6×10^{-6} .

The shape of the expansion curve of "Kovar" below and above its inflexion point is almost exactly that of several hard glasses and therefore, "Kovar" is the most suitable and the most used alloy for bonding and sealing hard glasses.

The operations involved in making a glass-metal seal or bonding are simple: glass and metal are brought into contact at a temperature which is high enough for the glass to be fluid and to wet the metal. In making a metal-glass bond, the metal is preferably preoxidized because the presence of an intermediate oxide layer between metal and glass is favourable to obtain glass-to-metal adherence. The bonding of this oxide layer with glass is ionic and metallic with metal.

The exception to the rule that the expansion coefficients must match, is the case where the metal is soft and thin so that its elastic limit is exceeded and a permanent set takes place without unduly stressing the glass.

Metal foils of 0.005 to 0.015 in thickness are considered thin enough to be used despite mis-matches in expansion coefficients. When the thickness is greater, there is not possibility actually to mis-match the expansion coefficients.

This important drawback is overcome by the use of a connecting part of variable composition made by powder metallurgy according to the present invention.

This is illustrated by the example of bonding a component of a hard glass to a component of austenitic steel with reference to the accompanying drawings.

In the drawings,

FIG. 1 is a diagram showing the expansion coefficient varying from that of hard glass (6×10^{-6}) to that

of austenitic steel (18×10^{-6}) for the temperature range $20^\circ \text{C.} - 500^\circ \text{C.}$

FIG. 2 shows a different part of the assembly:

$a-b$ is a compound of hard glass;
 $b-e$ is a connecting part with central part $c-d$ of variable composition made by powder metallurgy;
 $e-f$ is a component of austenitic steel made by conventional metallurgy.

FIG. 3 is a diagram showing the continuous and progressive composition (alloy system No. 1) of a connecting part from an alloy ("Kovar") 54% Fe, 29% Ni, 17% Co, 0% Cr (coefficient 6×10^{-6}) at the left hand end, to the composition of an austenitic steel (74% Fe, 18% Cr, 8% Ni, 0% Co) reached at the right hand end (coefficient 18×10^{-6}) of the connecting part.

These figures show that the left hand end of the connecting part match the expansion coefficient of the glass component and the right hand end part match the expansion coefficient of the austenitic steel component.

Therefore, bonding on both ends is made without stressing the glass and austenitic steel.

FIGURES 4 to 22 will be referred to more particularly hereinafter.

The difference between the expansion coefficients of two neighbouring sections in the transition part of the connecting part is so small that the stresses produced in the said sections by variations of temperature, during cooling after bonding or in service, are practically suppressed. The danger of cracks or of a rupture mainly in the glass component, is entirely avoided.

The bonding of ceramics, other than glass, to metal compounds, for example alumina, zirconia, steatite, forsterite, whitewares, offer similar features.

The ceramics and metal combinations of matching expansion coefficients are for example:

Ceramic	Metal	Coefficient of expansion	Range of temperature, $^\circ \text{C.}$
Forsterite-----	50% Ni, 50% Fe---	11×10^{-6}	20-700
Steatite-----	42% Ni, 58% Fe---	10×10^{-6}	20-700
Alumina-----	"Kovar"-----	9.3×10^{-6}	20-700
Zirconia-----	Molybdenum-----	6×10^{-6}	20-700

There are two well established methods of ceramic-to-metal bonding:

The molybdenum-manganese process which consists in applying a strongly adhering layer of metal to the ceramic and then brazing the metal member to this.

The active metal hydride process which consists in using an alloy of an active metal (Zr, Ti) which bonds directly the metal member to the ceramic in one operation.

The metal bonding agents used in the two methods are based on metals which have an affinity for chemical bonding with ceramics by reason of atom size or chemical properties.

As in the case of glass, the expansion coefficients of the ceramic and of the metal joined must match closely.

The use of a connecting part of variable composition according to the present invention makes possible the bonding of a ceramic component with a metal component even with greatly mismatching expansion coefficients, as for example: alumina to austenitic steel.

The connecting piece used for the combination hard glass-austenitic steel (FIGS. 1, 2 and 3) can be used also in this case because the hard glass and alumina have very similar expansion coefficients.

Assemblies of cermets with metals or alloys

Cermets are a group of materials comprising refractory carbides, nitrides, borides, silicides, oxides, aluminides, etc., with or without a cementing metal. The main interest in cermets is their very high chemical stability,

resistance to oxidation, high hardness and high hot strength. Generally, however, cermets have low resistance to thermal shocks.

Actually, the most important cermets are cemented carbides. The carbides used for tool materials can be divided on the basis of their applications into two large classes.

The first of these classes comprises, WC-Co compositions used for the machining of materials forming short chips, such as cast iron, glass and porcelain.

The second class are cemented multicarbides used for machinery materials which form long, continuous chips, e.g., steels of all types. According to the composition, WC-TiC-Co, WC-TaC(NbC)-Co and WC-TiC-TaC(NbC)-Co materials can be mentioned.

Nickel-bonded chromium carbide (Cr_3C_2) and also tungsten carbide (WC) bonded with corrosion resistant alloys (e.g., Cr-Ni) exhibit outstanding corrosion resistance and are used for parts working under conditions of severe wear and corrosion attack.

Titanium carbide is the only carbide which, in combination with binder metal, exhibits oxidation resistance and high strength at high temperature, as well as satisfactory resistance to thermal shocks.

A very large number of cemented-carbide compositions can also be used, for example:

Tungsten carbide with various binder metal other than Co, for example Ni-Cu, Ni-Cr, Ni-Mo, Co-W, Co-Mo-Cu, Fe-Ni-Cr.

Carbides with high melting point for example, carbides of hafnium, tantalum, zirconium, niobium and titanium. Tungsten-carbide free compositions, for example: TiC-VC-Ni material.

The bonding of cermets to metals is done by brazing. This operation is complicated by the great differences in thermal coefficients of expansion and by the difficulty in finding braze metals which will wet cermet surfaces. The need for brazes which are strong at high temperature (with high melting point) further increases the problem of differential expansion.

As machining speeds continue to increase, it may be advantageous, in certain cases not to make use of brazed tools, because the braze material would soften at the temperatures reached in the machining operation.

Thermal coefficient of expansion of the average carbide is usually about one half of the adjoining metal, usually steel. (5 to 8×10^{-6}) against (15×10^{-6}). These differences in the thermal expansion coefficient can easily create sufficient stresses during cooling from the brazing temperature, to result in fracture of the bond or cermet unless special precautions in method or design are taken. For example, for the brazing of larger tips or of complicated designs, as well as for brazing high TiC grade, the application of a compensation foil as an intermediate layer between the tip and the tool face is used (foil brazing or sandwich brazing).

Matching the coefficients of expansion is very helpful. When the tool shank is of a metal which matches the coefficient of the carbide type, for example "Kovar" or tungsten heavy alloy (90% W-7% Ni-3% Cr) the carbide tips can be brazed by conventional methods, using almost any braze that will wet the carbide. The resultant tool has few residual stresses and is crackfree.

The hard and soft solder are used for brazing cemented-carbide tips. When the cutting temperature is high, copper solder, Cu-Ni brazes, are used. The cermets containing large percentages of titanium carbide are adequately wet by palladium-nickel alloys (for example 60% Pd-40% Ni).

It is to be noted that the brazes have not always the necessary corrosion resistance, for example copper braze in contact with liquid sodium.

Because of such brazing problems, many users have

switched to mechanical tools. But the latter technique has also its own problems and limitations.

The elimination of brazed joints can be successfully achieved by the use of a connecting part of variable composition according to the present invention.

By the use of the seven basic alloy systems above mentioned, the bonding of the cemented carbides components to the compounds of ferritic steels, superalloys and austenitic steel can be done without difficulty.

The most useful alloy-system is the system of tungsten carbide cemented with variable content of cobalt (from 0 to 100%) which can match the expansion coefficient as low as 4.5×10^{-6} of tungsten or of tungsten carbide with 4.5% Co which has the higher hardness and brittleness and is therefore very difficult to braze to steel. In the WC-Co system with increasing percentage of cobalt, lower hardness is associated with high strength and higher toughness, which is an important advantage. The following example illustrates the bonding of a tungsten carbide component with 4.5% Co, to a carbon steel component.

FIG. 4 of the accompanying drawings is a diagram showing the expansion coefficient varying from that of tungsten carbide with 4.5% Co (5×10^{-6}) to that of carbon steel (15×10^{-6}) for a temperature range of 200–700° C.

FIG. 5 shows the assembly of tungsten carbide with a cobalt component (a–b) united with carbon steel component (f–g) united by a connecting part (b–f) of varying composition between c and e. The two components and the connecting parts are made by powder metallurgy which allows of obtaining the said assembly as a monobloc piece without any joint.

FIG. 6 shows the possibility of making the assembly by bonding the two components and the two members of the connecting part, separately made, and this for economical or technical reasons. The bonding of the joints b and d can be effected by brazing and that of the joint f by flash welding. Owing to the matching expansion coefficients in the joints b, d, f, the three bondings can be carried out without difficulty. The carbon steel component is in this case made by conventional metallurgy.

FIG. 7 is a diagram showing the compositions of Cemented tungsten carbide component 89.6% W, 5.8% C, 4.5% Co;

Connecting parts of variable composition comprising two alloy systems;

Alloy system No. 4 from 89% W, 5.8% C, 4.5% C. (5×10^{-6}) to 49.8% W, 3.2% C, 47% C (9.3×10^{-6}); Alloy system No. 1 from 54% Fe, 29% Ni, 17% Co, 0% Cr (9.3×10^{-6}) to 65% Fe, 17% Ni, 11% Cr, 7% Co (15×10^{-6});

Carbon steel component; the line 100% is for the composition 99% Fe, 0.25% C, 0.35% Si, 0.4% Mn.

The bonding of cemented carbide of titanium of high strength at high temperature to heat-resisting superalloys is a difficult operation to carry out because of mis-matches in the expansion coefficients of the two materials.

The difficulty can be easily overcome by the present invention as illustrated in the following drawings, showing an assembly of cemented titanium carbide and "Nimonic 90" nickel-based superalloy.

FIG. 8 is a diagram showing the expansion coefficient varying from that of the cemented carbide (10.2×10^{-6}) to that of "Nimonic 90" (15×10^{-6}) for the temperature range of 20° C. to 700° C.

FIG. 9 shows the assembly obtained as a monobloc piece by powder metallurgy.

FIG. 10 shows the assembly divided into three parts separately prepared and ready for bonding. The "Nimonic 90" component represented is made by conventional metallurgy.

FIG. 11 is a diagram showing:

The line 100% (a–b) for the composition of the

cemented titanium carbide: 52.1% Ti, 1.7% Nb, 0.3% Ta, 13.1% C, 30% Ni.

The connecting part of alloy system No. 1 of a composition varying from 56% Fe, 27% Ni, 15.5% Co, 1.5% Cr (10.2×10^{-6}) to 65% Fe, 17% Ni, 7% Co, 11% Cr (15×10^{-6});

The line 100% (e–f) is for the composition of "Nimonic 90" 0.1% C, 1% Si, 4% Fe, 0.5% Mn, 20% Cr, 2.9% Ti, 1.5% Al, 18% Co, 48% Ni.

Assemblies of heavy alloys with metals or alloys

The heavy alloys based on tungsten and made by powder metallurgy have interesting characteristics: high density, good mechanical properties, high absorption of X-rays.

By reason of the high density, they are used as balancing masses permitting to obtain a maximum inertia with a minimum volume. Examples of application: rotors for gyroscopes, inertia masses for rocket mechanisms.

The most used heavy alloy has the composition 92% W, 5% Ni, 3% Cu which is also used for the alloy system No. 6.

Other compositions are also used for example: W-Ni-Fe, W-Ni-Cr, W-Ni-Cu-Mo.

Owing to the very low expansion coefficient of 7.2×10^{-6} and rather low ductility of the heavy alloy, its bonding to the austenitic steel, with high expansion coefficient of 19×10^{-6} – 22.2×10^{-6} is practically impossible to obtain by the known methods.

Such a difficulty is overcome by the use according to the present invention of a connecting part comprising three basic alloys Nos. 6, 1 and 7 and bridging the large gap between the expansion coefficient of 7.2×10^{-6} and 22×10^{-6} .

This is illustrated in the following drawings:

FIG. 12 is a diagram showing the expansion coefficient varying from that of the heavy alloy (7.2×10^{-6}) to that of the austenitic steel (22.2×10^{-6}) for the temperature range of 20° C.–700° C.

FIG. 13 shows a complicated assembly realised as a monobloc piece by powder metallurgy.

FIG. 14 shows the assembly divided into their individual components which can be bonded easily owing to the matching coefficient of expansion of the joint b, d, e and g. The austenitic component represented is made by conventional metallurgy.

FIG. 15 is a diagram showing the composition of Heavy alloy component: 92% W, 5% Ni, 3% Cu (7.2×10^{-6}),

Connecting part comprises three alloy systems:

Alloy system No. 6: from 92% W, 5% Ni, 3% Cu (7.2×10^{-6}) to 68% W, 30% Ni, 2% Cu (9.3×10^{-6});

Alloy system No. 1: from 54% Fe, 29% Ni, 17% Co (9.3×10^{-6}) to 74% Fe, 18% Cr, 8% Ni (19×10^{-6});

Alloy system No. 7: from 74% Fe, 18% Cr, 8% Ni (19×10^{-6}) to 79.5% Fe, 3.5% Cr, 12% Ni, 5% Mn (22.2×10^{-6});

Austenitic steel component: 79.5% Fe, 3.5% Cr, 12% Ni, 5% Mn (22.2×10^{-6}).

Assemblies of brittle materials with each other

The assemblies of brittle materials such as ceramics and cermets having different thermal expansion coefficients, is a very difficult problem.

This problem can be solved by the present invention as shown by the following example illustrating the assembly of a brittle cermet consisting of cemented tungsten carbide with only 4.5% Co and a brittle ceramic consisting of alumina.

FIG. 16 is a diagram showing the expansion coefficient varying from that of the cemented tungsten carbide (5×10^{-6}) to that of alumina (9.3×10^{-6}) for the temperature range 20° C.–700° C.

FIG. 17 shows the assembly comprising a cermet component and the connecting part made in one piece (a-e) by powder metallurgy, bonded to the alumina component (e-f).

FIG. 18 is a diagram showing the composition of A cermet component: 89.7% W, 5.8% C, 4.5% C (5×10^{-6});

A connecting part made of an alloy system No. 4: from 89.7% W, 5.8% C, 4.5% Co, (5×10^{-6}) to 49.8% W, 3.2% C, 47% Co (9.3×10^{-6});

A ceramic component: line 100% is for an alumina composition having a high percentage of Al_2O_3 .

Assemblies of more than two components

The present invention allows of making assemblies of more than two components by the use of two or more connecting parts of variable composition, as shown in the following drawings illustrating an assembly of three components and two connecting parts.

FIG. 19 is a diagram showing the expansion coefficient varying from that of alumina component (9.3×10^{-6}) to that of "Nimonic 90" (15×10^{-6}), and then to that of the cermet (10.2×10^{-6}) for the temperature range $20^\circ C.$ – $700^\circ C.$

FIG. 20 shows the assembly comprising an alumina component bonded with a sub-assembly in one piece made by powder metallurgy including two components (e-f) and (i-j) and two connecting parts (b-e) and (f-i).

FIG. 21 shows the assembly effected by bonding the individual components and connecting parts. The "Nimonic" central component is made by conventional metallurgy.

FIG. 22 is a diagram showing the composition of A first component alumina: the line 100% is for the composition of high % of Al_2O_3 ;

A first transition part—alloy system No. 1, from 54% Fe, 29% Ni, 17% Co (9.3×10^{-6}) to 65% Fe, 17% Ni, 11% Cr, 7% Co (15×10^{-6});

A second component "Nimonic 90": 0.1% C, 1% Si, 4% Fe, 0.5% Mn, 20% Cr, 2.9% Ti, 1.5% Al, 18% Co, 48% Ni;

A second transition part—alloy system No. 1, from 65% Fe, 17% Ni, 11% Cr, 7% Co (15×10^{-6}) to 56% Fe, 27% Ni, 1.5% Cr, 15.5% Co (10.2×10^{-6});

A third component: cemented titanium carbide, 52.1% Ti, 1.7% Nb, 0.3% Ta, 13.1% C, 30% Ni.

The resistance to high temperature of the seven basic alloy systems for a connecting part made by powder metallurgy may be increased by means of a small addition of C and elements such as Mo, W, V, Ti, Al, Nb, B, which form carbides and intermetallic compounds, or by means of the addition of oxides, silicides and nitrides.

The bonding of two dissimilar metals or alloys A and B having the same expansion coefficients, may be difficult to carry out for some metallurgical reasons, for example reduced miscibility due to the great difference in atomic diameters (unfavorable size factor) or by formation of a brittle intermetallic compound.

In such a case, a third material C, inserted between A and B, with matching expansion coefficient and chosen for its compatibility with A and B, may give a satisfactory bonding.

The present invention is very suitable for such a technique.

The assemblies made according to the present invention may have any geometrical form, including rods, tubes, sheets, etc.

The present invention gives a practical solution to the difficult problems of making assemblies with brittle materials of mis-matching expansion coefficients.

What I claim is:

1. A composite structure comprising two spaced apart component parts and a connecting piece metallurgically bonded between said component parts:

(A) said component parts being selected from the group consisting of:

- (1) ceramics and metals,
- (2) cermets and metals,
- (3) cermets and super alloys,
- (4) heavy tungsten alloys and metals,
- (5) ceramics and cermets, and
- (6) ceramics and super alloys,

(B) said connecting piece being at least one alloy formed by powder metallurgy and having a coefficient of expansion which varies substantially continuously from one end to the other and in which said coefficient of expansion at each end of said connecting piece substantially matches the coefficient of expansion at the adjacent end of the component part to which it is bonded, the alloy of said connecting piece consisting essentially of a combination of the hereinafter specified elements, the amount of each specified element in the alloy varying substantially continuously from one end to the other within the indicated range, said alloys being selected from the group consisting of:

- (a) an alloy consisting essentially of iron over the range of 54 to 74%, nickel over the range of 29 to 8%, cobalt over the range of 17 to 0%, and chromium within the range of 0 to 18%;
- (b) an alloy consisting essentially of iron over the range of 58 to 74%, nickel over the range of 42 to 8%, and chromium over the range of 0 to 18%;
- (c) an alloy consisting essentially of zirconium over the range of 100 to 0%, and titanium over the range of 0 to 100%;
- (d) an alloy consisting essentially of tungsten over the range of 94 to 0%, carbon over the range of 6 to 0%, and cobalt over the range of 0 to 100%;
- (e) an alloy consisting essentially of titanium over the range of 81.5 to 0%, carbon over the range of 18.5 to 0%, and nickel over the range of 0 to 100%;
- (f) an alloy consisting essentially of tungsten over the range of 92 to 0%, nickel over the range of 5 to 100%, and copper over the range of 3 to 0%, and
- (g) an alloy consisting essentially of iron over the range of 74 to 79.5%, chromium over the range of 18 to 3.5%, nickel over the range of 8 to 12%, and manganese over the range of 0 to 5%.

2. A structure in accordance with claim 1 wherein the component parts are a ceramic and a metal.

3. A structure in accordance with claim 2 wherein the ceramic is hard glass, the metal is austenitic steel and the connecting piece is alloy (a).

4. A structure in accordance with claim 1 wherein the component parts are a cermet and a metal.

5. A structure in accordance with claim 4 wherein the cermet is cemented tungsten carbide having 4.5% cobalt, the metal is carbon steel and the connecting piece is alloy (d), connected to alloy (a).

6. A structure in accordance with claim 1 wherein the component parts are a cermet and a super alloy.

7. A structure in accordance with claim 6 wherein the cermet is cemented titanium carbide, the super alloy is a nickel-based super alloy and the connecting piece is alloy (a).

8. A structure in accordance with claim 1 wherein the component parts are a heavy tungsten alloy and a metal.

9. A structure in accordance with claim 8 wherein the heavy alloy is a tungsten-based heavy alloy, the metal is austenitic steel and the connecting piece is alloy (f) connected to alloy (a), which in turn is connected to alloy (g).

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10. A structure in accordance with claim 1 wherein the component parts are a ceramic and a cermet.

11. A structure in accordance with claim 10 wherein the ceramic is alumina, the cermet is cemented tungsten carbide having 4.5% cobalt and the connecting piece is alloy (d).

12. A structure in accordance with claim 1 wherein the component parts are a ceramic and a super alloy.

13. A structure in accordance with claim 12 wherein the ceramic is alumina, the super alloy is a nickel-based super alloy and the connecting piece is alloy (a).

14. A structure in accordance with claim 1 wherein each of the connecting pieces contains a material se-

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lected from the group consisting of carbon and an element selected from the group consisting of molybdenum, tungsten, vanadium, titanium, aluminum, niobium, or boron; oxides; silicides; or nitrides in a minor amount sufficient to improve the resistance to high temperature of said connecting piece.

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