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(54) **ARTICLE COMPRISING IMPROVED NOBLE METAL-BASED ALLOYS AND METHOD FOR MAKING THE SAME**

of provisional application No. 60/161,290, filed on Oct. 25, 1999 and which is a non-provisional of provisional application No. 60/161,291, filed on Oct. 25, 1999.

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(57) **ABSTRACT**

A device having electrical contacts formed from an alloy having improved wear resistance is provided, the alloy being particularly useful in microrelay devices formed by MEMS technology. In one embodiment, the alloys are chosen to allow sufficient precipitation hardening to improve wear resistance, but keep precipitation below a level that would unacceptably reduce electrical conductivity. This is achieved by using alloying materials that have very limited or no solid solubility in the noble metal matrix, e.g., less than 4 wt. % solid solubility. In a second embodiment, an alloy contains a noble metal matrix and insoluble, dispersoid particles having no solubility in the matrix, these dispersoid particles offering a similar strengthening mechanism.

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(22) Filed: **Dec. 6, 2000**

Related U.S. Application Data

(60) Division of application No. 09/484,627, filed on Jan. 18, 2000, now abandoned, which is a non-provisional

FIG. 1

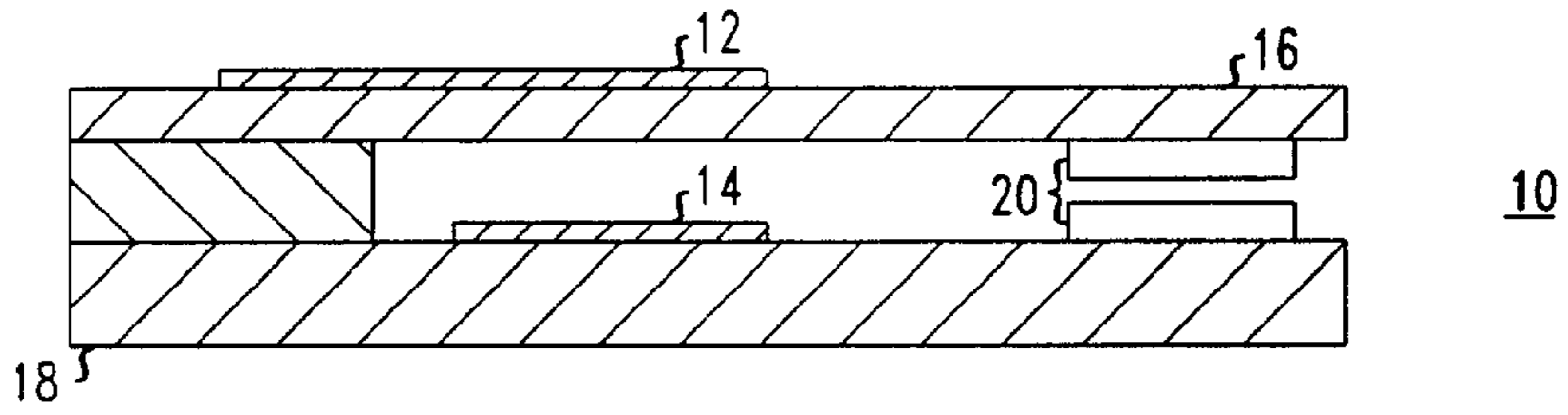


FIG. 2A

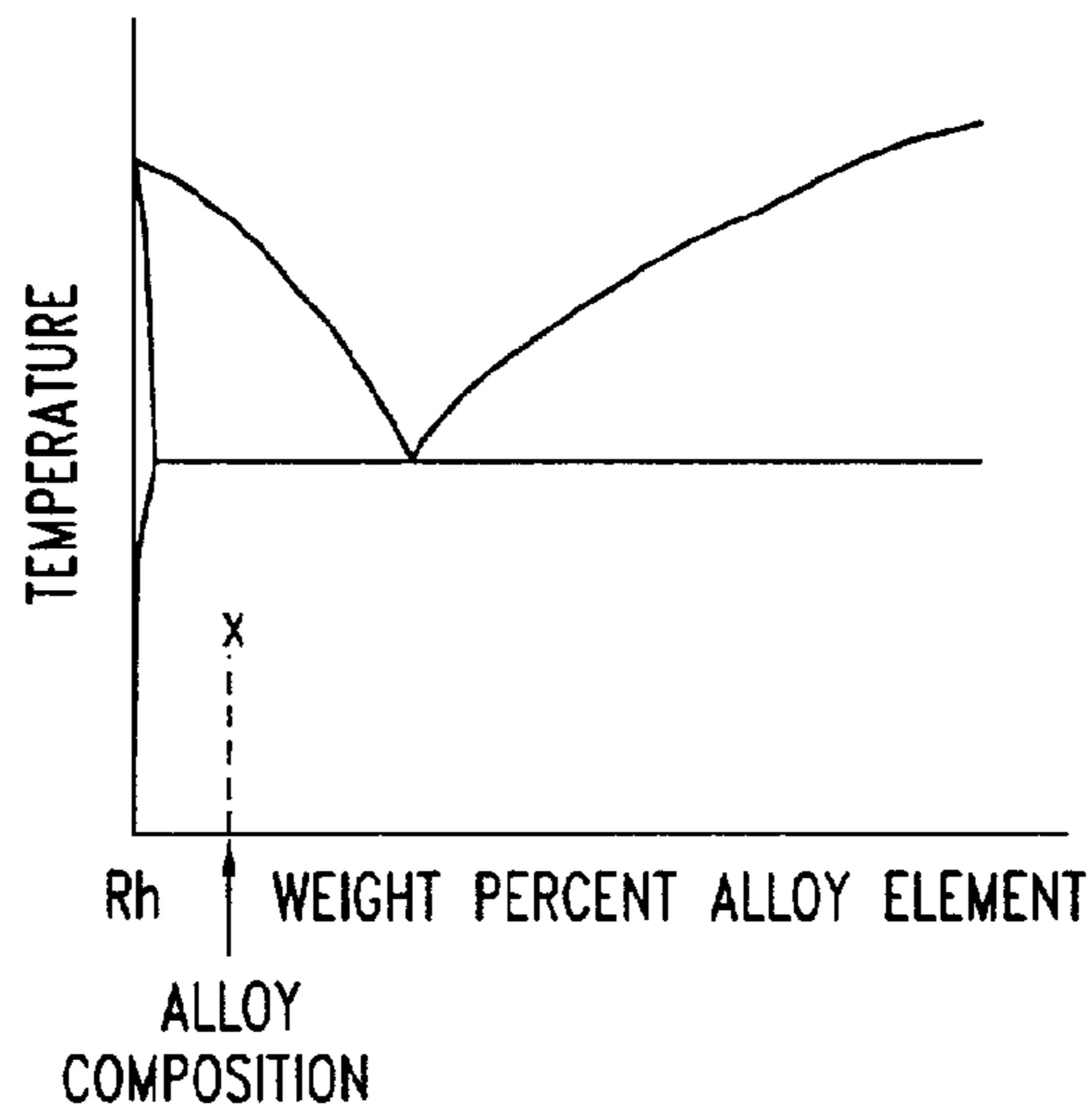


FIG. 2B

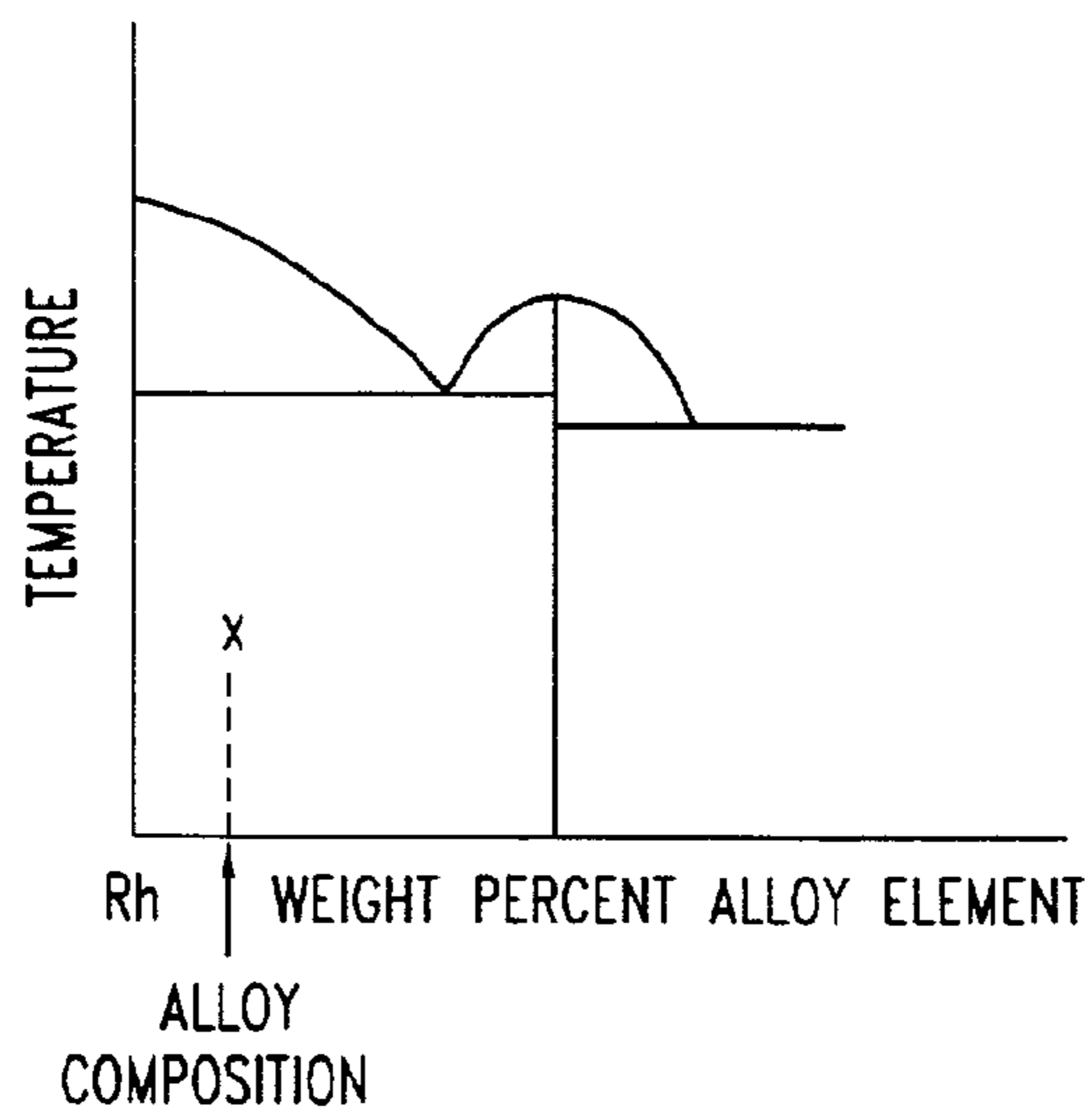


FIG. 3 A

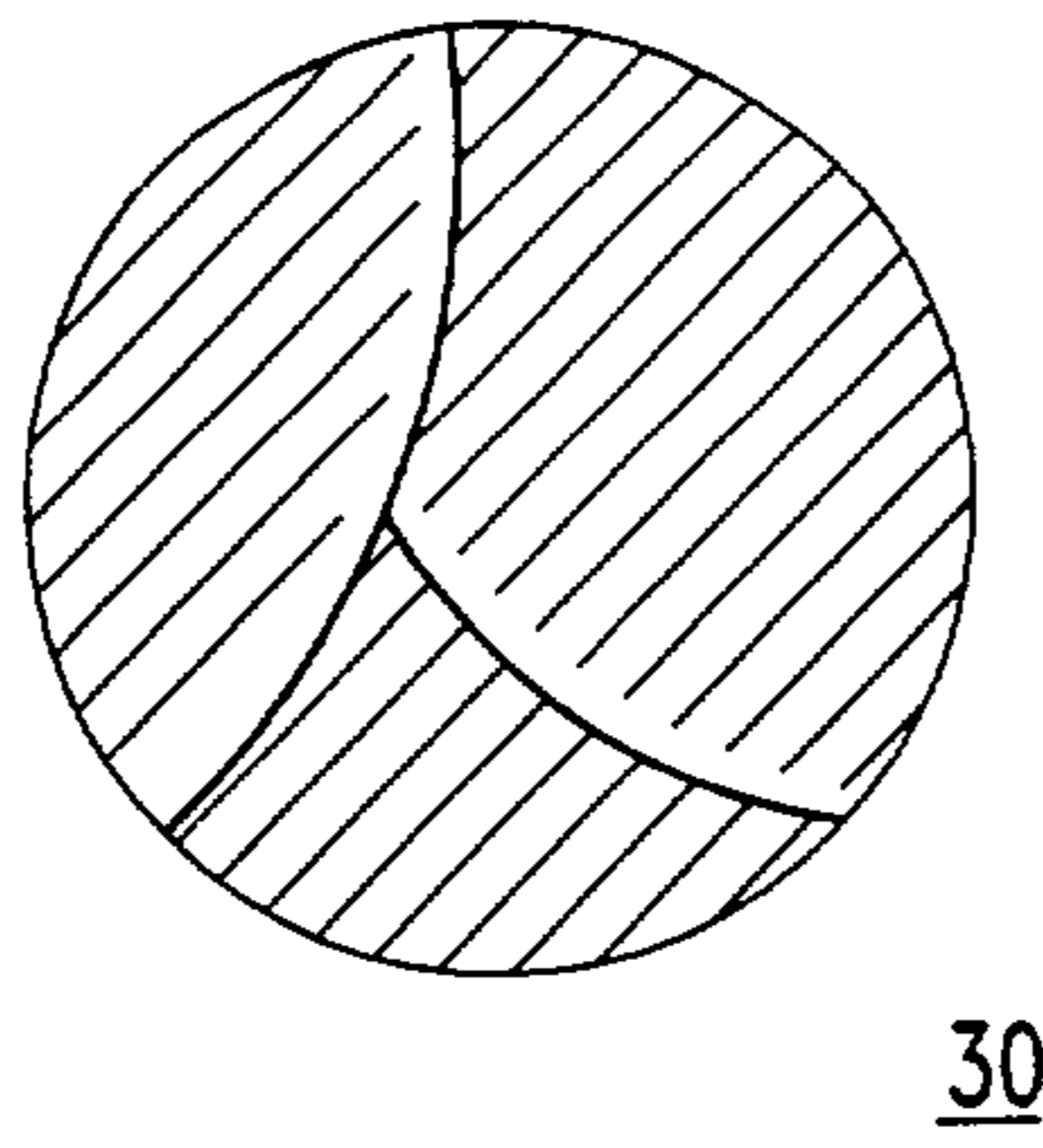


FIG. 3 B

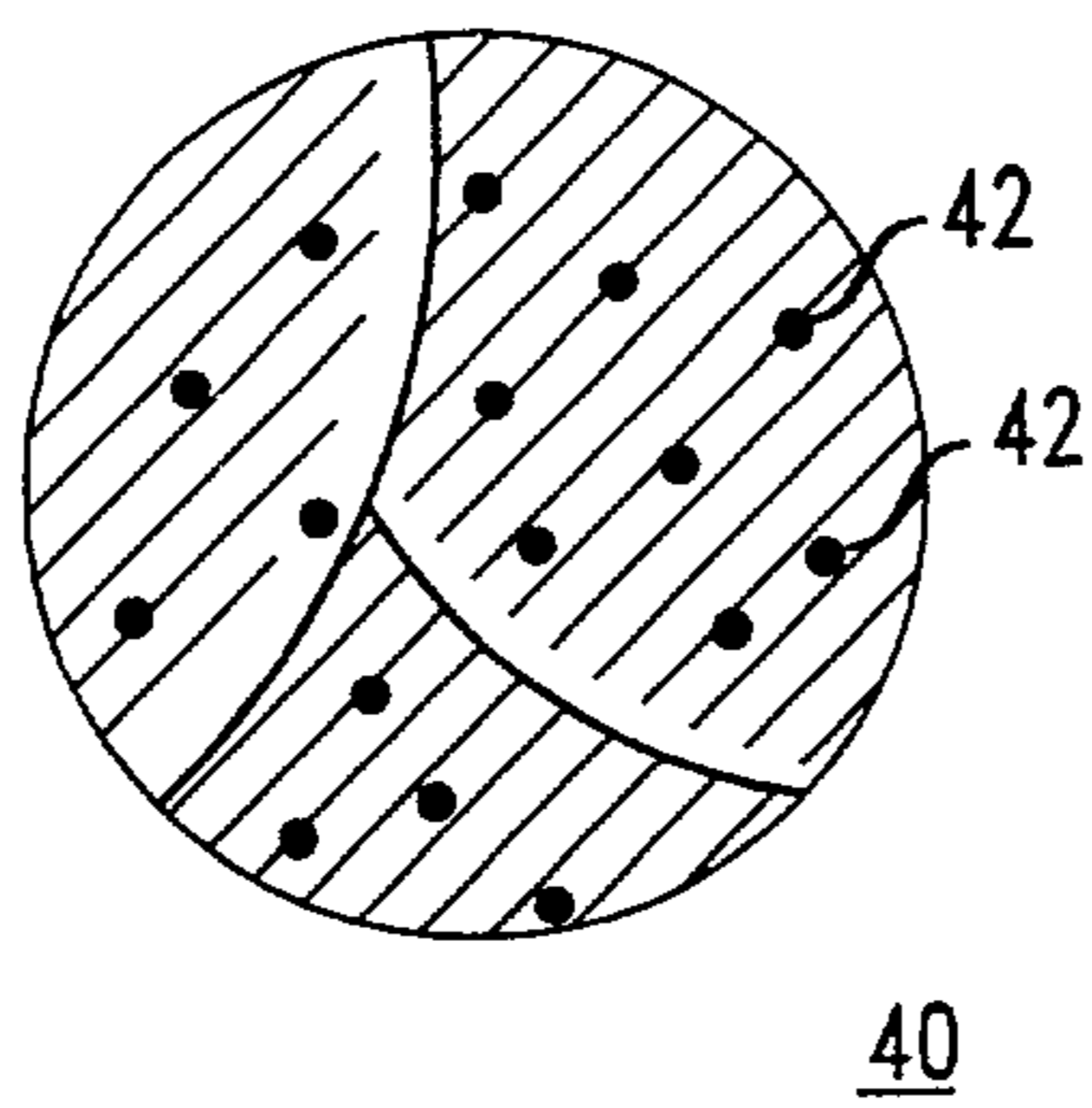


FIG. 4

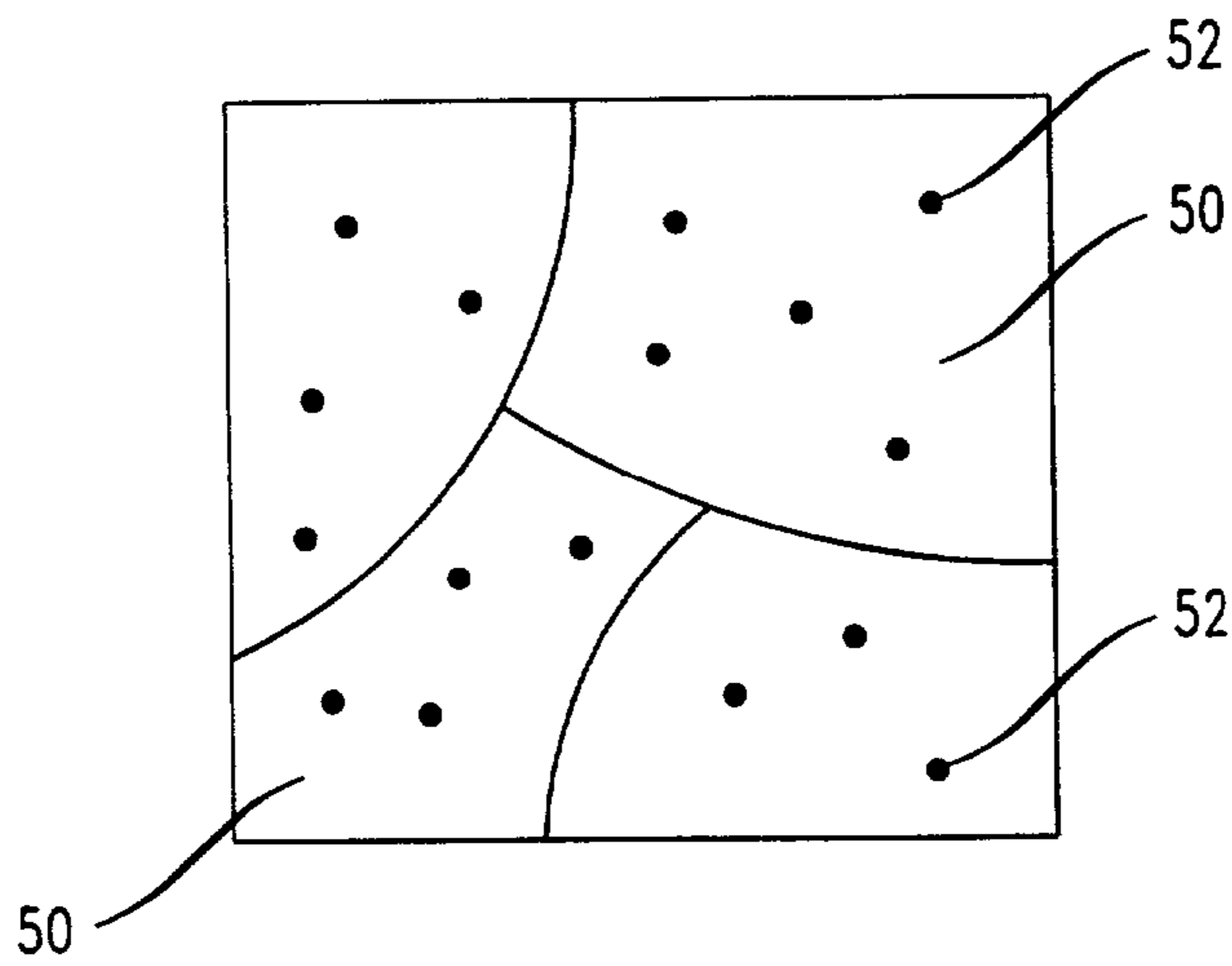


FIG. 5

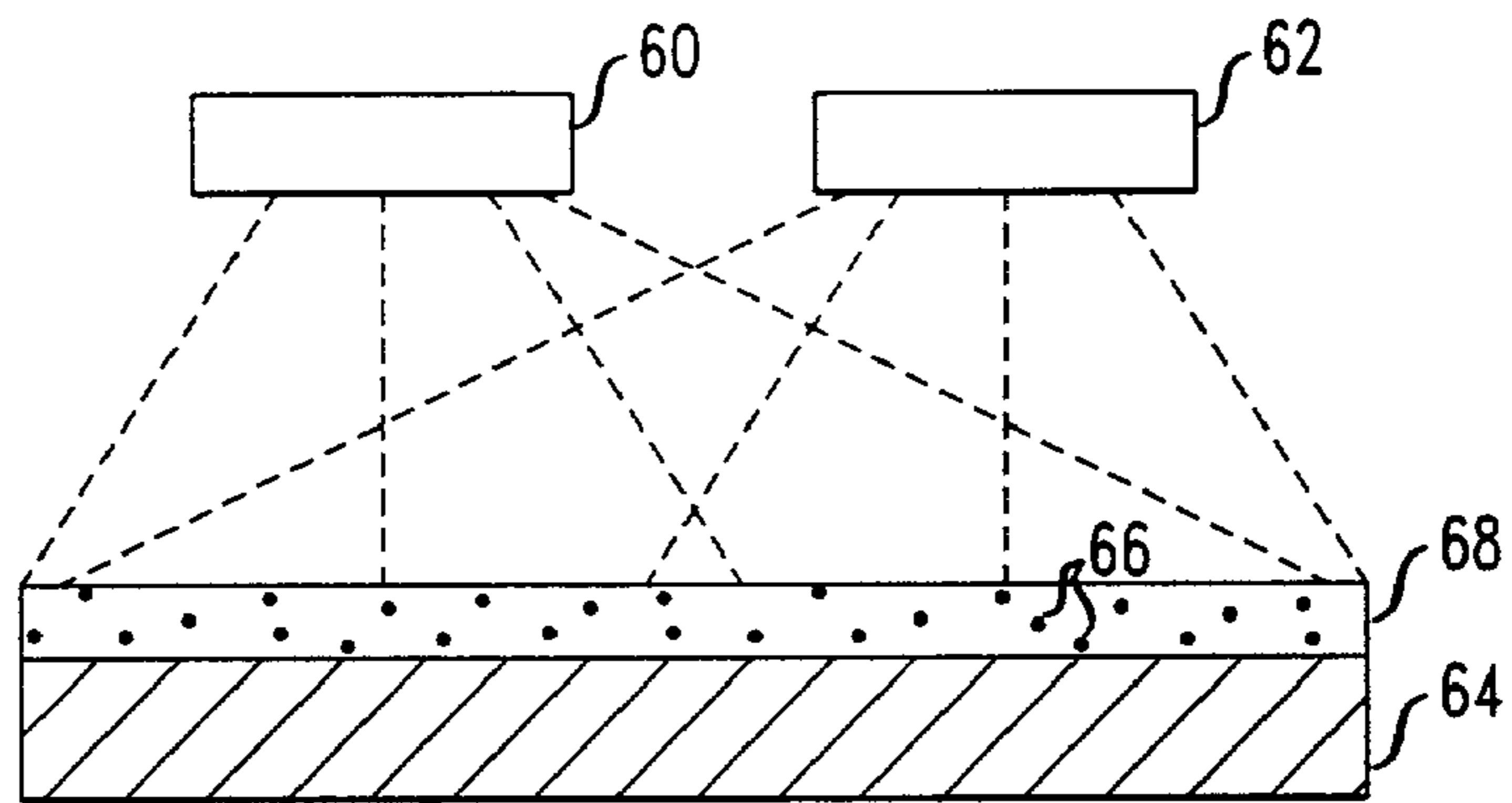


FIG. 6

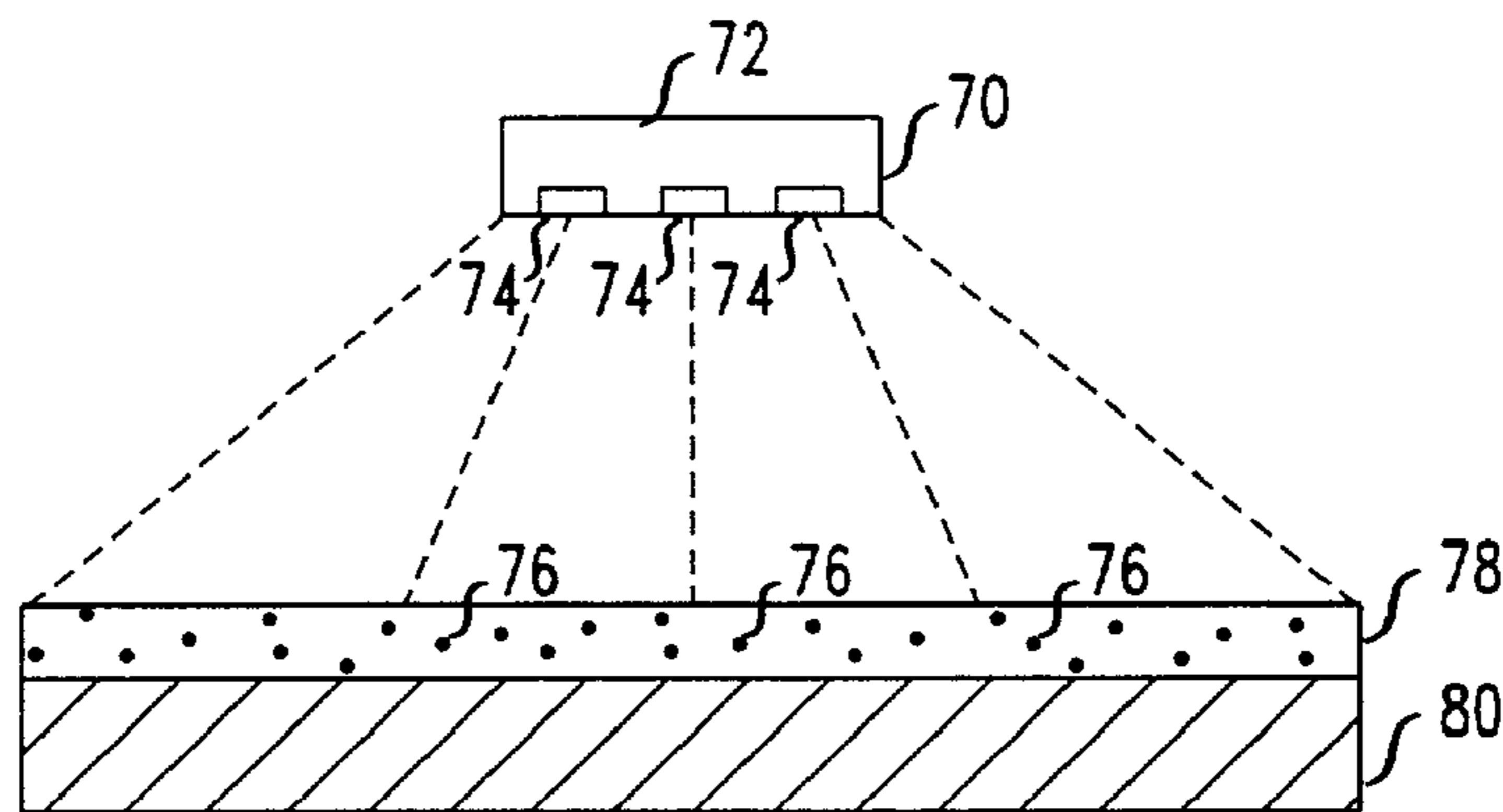
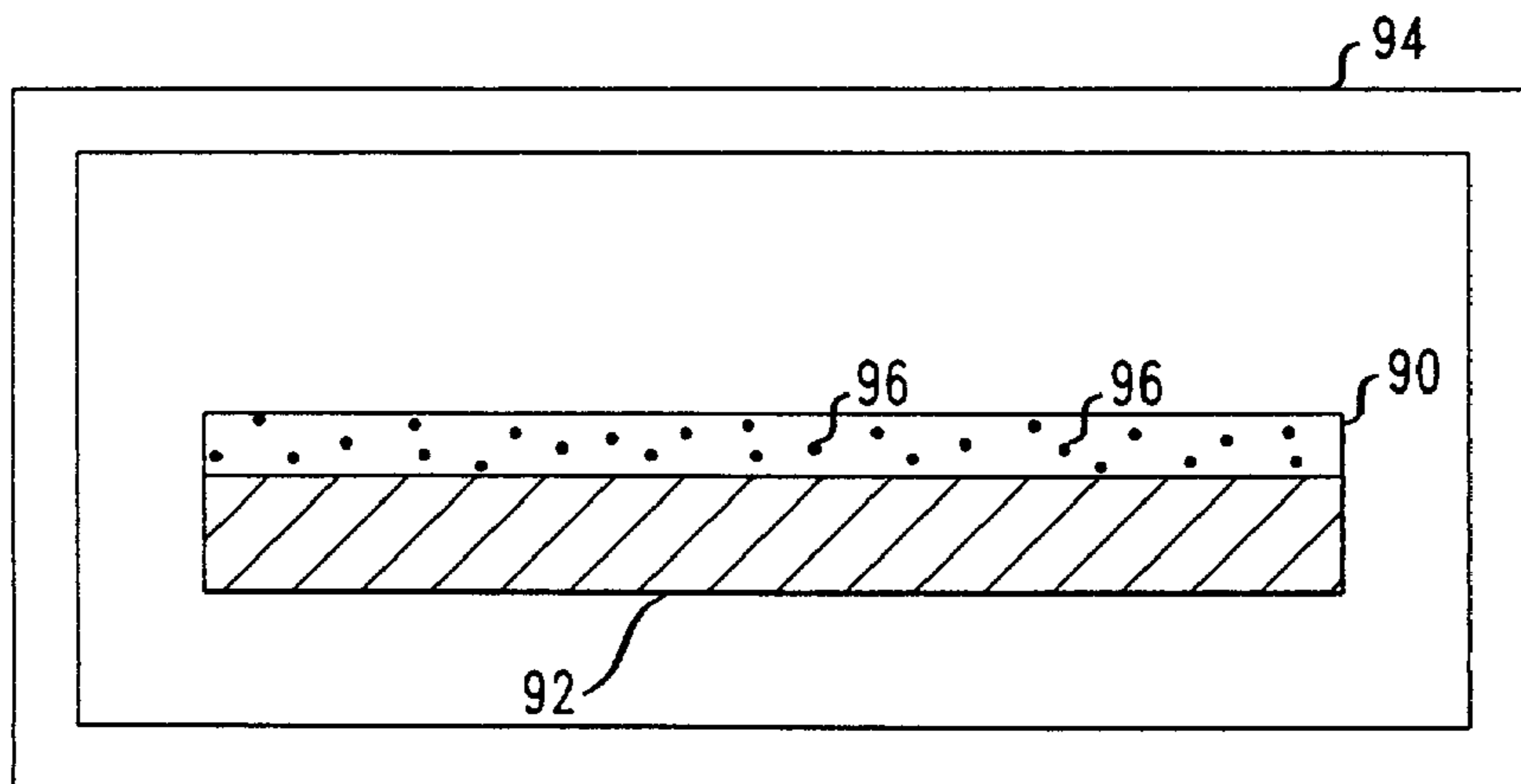


FIG. 7



**ARTICLE COMPRISING IMPROVED NOBLE
METAL-BASED ALLOYS AND METHOD FOR
MAKING THE SAME**

CROSS-REFERENCE TO RELATED
APPLICATIONS

[0001] This application claims priority of Provisional application Ser. No. 60/161290 which was filed Oct. 25, 1999 and Provisional application Ser. No. 60/161291 which was filed Oct. 25, 1999.

BACKGROUND OF THE INVENTION

[0002] 1. Field of the Invention

[0003] The invention relates to devices comprising electrical contact materials, in particular, high-speed switching relays, including relays based on microelectromechanical systems (MEMS).

[0004] 2. Discussion of the Related Art

[0005] High-speed switching relays are useful in a variety of applications in automatic test equipment, automotive technologies, and telecommunications technologies—e.g., signal routers, impedance matching networks, and tunable filters. Today, microrelays can be manufactured by microelectromechanical systems (MEMS) technology. In this technology, devices and components are fabricated from silicon using well-developed techniques related to integrated circuit processing. Microelectromechanical relays are receiving increased attention because of their advantages over conventional relays—i.e., smaller size and less power consumption. In addition, their potential is being realized in the integration of these systems with electronics, where large numbers of relays can exist on a single chip that may contain other electronics as well.

[0006] The advantages of MEMS microrelays over semiconductor switches include lower on-resistance, higher off-resistance, higher dielectric strength, lower power consumption, and lower cost. (S. Hanno et al., *Proceeding of the International Symposium on Microsystems, Intelligent Materials and Robots 7th Symposium*, 173-176 (1995)) Specifically, conventional switches using transistors have relatively low breakdown voltage (e.g., 30 V) and relatively low off-resistance (50 kilo-Ohms at 100 MHz), as discussed in U.S. Pat. No. 5,578,976. Solid state switches tend to exhibit large on-state loss and poor off-state isolation. In addition to replacing conventional relays, microrelays have the potential to replace traditional solid state devices in significant markets. In addition, complex switching arrays and devices designed to accommodate high-frequency signals with low loss are a natural extension for such MEMS relays.

[0007] Switches for telecommunications applications require a large dynamic range between on-state and off-state impedance, in the RF regime. Achieving a large on/off impedance ratio requires good electrical contact with minimal resistance when the switch is on (closed circuit) and low parasitic capacitive coupling when the switch is off (open circuit). Mechanical switches with metal-to-metal contact are still preferred where low insertion loss and high off-isolation are required, particularly in cost-sensitive applications. A key to the success of these relays is reliable, wear-resistant contact materials.

[0008] Historically, gold alloys have been successful in electrical contact materials for reed switches (R. G. Baker and T. A. Palumbo, *Plating and Surface Finishing*, 70, 63-66 (1983)). This is especially true for applications requiring low-force, low voltage contacts that cannot tolerate the buildup of tarnish films that can modify contact resistance. However, microrelay switches are expected to experience billions of on-off cycles. This design expectation renders soft materials, like pure gold, ineffective, e.g., because of local welding and stiction problems caused by friction and wear. As a result, new materials must be developed to provide good electrical contact and wear-resistance. Noble metal contact materials and their alloys, while possessing desirably low electrical resistivities and oxidation resistance, are not always suited for the sliding low-voltage low-current electrical contacts used in MEMS microrelay switches. In particular, wear resistance is often questionable. Thus, improved noble metal alloys are desired as contact materials for reliable microrelay switches.

SUMMARY OF THE INVENTION

[0009] The invention provides a device having electrical contacts formed from an alloy having improved wear resistance. The contact alloy is particularly useful in microrelay devices formed by MEMS technology.

[0010] The alloy contains at least one noble metal, such as rhodium, platinum, palladium, gold, or ruthenium. (Noble metals includes Au, Ag, Pt, Pd, Ir, Rh, Ru, Os.) Noble metals are known to be useful as contact materials due to high oxidation- and corrosion-resistance and reasonable electrical conductivity. But because the contact materials in microrelay devices typically undergo billions of cycles of contact involving friction and wear, the contact materials must meet extremely high standards for wear resistance. By selecting particular alloying elements, along with providing a particular microstructure, it is possible to attain such higher wear resistance and still maintain a suitable electrical conductivity.

[0011] In one embodiment, the alloys are chosen to allow sufficient precipitation hardening to improve wear resistance, but keep precipitation below a level that would unacceptably reduce electrical conductivity. This is achieved by using alloying materials that have very limited or no solid solubility in the noble metal matrix, e.g., less than 4 wt. % solid solubility. The low solubility reduces the extent to which the conductivity will be compromised by conventional alloying effects, i.e., deterioration of the electrical conductivity due to solute atoms. And the low solubility also reduces the extent to which the second phase (precipitates) are able to coarsen (grow) during heat treatment, repeated contact operations, and similar processes. Yet, it is still possible to form sufficient precipitates in the noble metal matrix to achieve the desired mechanical strengthening and wear resistance. The resulting alloy exhibits a mechanical hardness at least 30% higher than the noble metal matrix alone.

[0012] In a second embodiment, an alloy contains a noble metal matrix and insoluble, dispersoid particles, which offer a similar strengthening mechanism—e.g., mechanical hardness at least 30% higher than the noble metal matrix alone. (Insoluble indicates a material having less than 0.01 wt. % solubility in the noble metal matrix.) Examples of dispersoid

particles include oxides, nitrides, and carbides. Because the dispersoids have essentially no solubility in the matrix, the particles remain in the matrix to impede the motion of dislocations and grain boundaries, thereby strengthening the material.

BRIEF DESCRIPTION OF THE DRAWINGS

[0013] **FIG. 1** illustrates an embodiment of a microelectromechanical (MEMS) based microrelay.

[0014] **FIG. 2A** illustrates a two component temperature-composition phase diagram, reflecting limited solid solubility of the alloying element.

[0015] **FIG. 2B** illustrates a two component temperature-composition phase diagram with essentially no solid solubility of the alloying element, reflecting the creation of an intermetallic phase upon annealing, according to a first embodiment of the invention.

[0016] **FIG. 3A** schematically illustrates the microstructure of a supersaturated noble-metal based alloy of one embodiment of the invention, in an as-deposited state.

[0017] **FIG. 3B** schematically illustrates the microstructure of a noble-metal based alloy of one embodiment of the invention, after precipitation heat treatment.

[0018] **FIG. 4** schematically illustrates the microstructure of a dispersoid containing alloy according to a second embodiment of the invention.

[0019] **FIG. 5** illustrates a process useful for forming an alloy according to the second embodiment of the invention.

[0020] **FIG. 6** illustrates another process useful for forming an alloy according to the second embodiment of the invention.

[0021] **FIG. 7** illustrates a further process useful for forming an alloy according to the second embodiment of the invention.

DETAILED DESCRIPTION OF THE INVENTION

[0022] Microelectromechanical relays offer the advantage of being smaller and consuming less power than conventional larger-scale relays. These relays perform an electrical function of connecting electrical paths for current to traverse, by actuation and bending of a cantilever-type switching arm such that circuit connection occurs at contacts made of specialized contact materials. Repeated contact at these contact points and the continual emission of current demand careful selection and fabrication of contact materials. The invention involves use of particular contact materials containing alloyed noble metals, the alloying and associated microstructure allowing attainment of greater mechanical strength with a lower loss of conductivity as compared to conventional alloying.

[0023] **FIG. 1** schematically illustrates a microelectromechanical microrelay device **10** of the invention. In this device, an electrostatic voltage is applied between the beam electrode **12** and the actuator electrode **14**, which induces an attractive force and closes the gap between the cantilever **16** and the substrate **18**. This movement of the cantilever **16** connects the electrical circuit by bringing the two contact pads **20** together. The low-resistivity contact pads **20**,

formed from particular wear-resistant alloys of the invention, provide relatively low power loss and time-dependant degradation. In this embodiment, the switch is fabricated on a silicon substrate using conventional microfabrication techniques such as masking, etching, lift-off and deposition. (See, e.g., M. J. Madou, *Fundamentals of microfabrication*, (1997) ISBN 0-8493-9451-1.) The switch components are formed by thin-film deposition buildup or by etching away surrounding material. The actuating part is composed of a cantilever arm **16**, typically formed from semiconducting or insulating material, such as silicon, silicon dioxide or silicon nitride, for example. The contact pads **20** are deposited on part of the substrate as well as on part of the mating cantilever. According to the invention, one or both of the pads **20** are formed using a thin film of the noble-metal alloy, as described in more detail below.

[0024] Noble metals, such as rhodium, platinum, palladium, gold, ruthenium, and silver, are useful as contact materials because these elements offer high oxidation- and corrosion-resistance and reasonable electrical conductivity. For instance, these materials have been used successfully in the reed switch industry. However, according to the invention, improved contact materials are obtained by alloying and processing such noble metals in a particular manner. Rhodium, for example, exhibits relatively good wear resistance, reasonable electrical conduction properties, relatively high mechanical strength and a high melting temperature (1966°C.). While these properties all indicate the usefulness of rhodium for contact materials, the contact materials in microrelay devices typically undergo billions of cycles of contact involving friction and wear. Increased wear-resistance is therefore desired.

[0025] In a first embodiment, the invention addresses this need by alloying and precipitation hardening of such noble metals. The resulting alloys exhibit high mechanical strength due to the precipitation hardening, yet with relatively low conductivity loss due to solid-solution-induced effects. (As known in the art, creation of a solid-solution tends to reduce conductivity of the matrix material.) In particular, the alloying materials for use with noble metals have very limited or no solid solubility in the noble metal matrix. The advantages of selecting alloys with very low solubility limits are two-fold. First, the low solubility reduces the extent to which the conductivity will be compromised by conventional alloying effects, i.e., substantial deterioration of the electrical conductivity of elemental metals due to addition of solute atoms. Second, the low solubility reduces the extent to which the second phase (precipitates) are able to coarsen during heat treatment, repeated contact operations, local heating, exposure to ambient temperature rise, and similar environmental changes. Such coarsening is undesirable because of potential deterioration of mechanical hardness and wear resistance.

[0026] For example, **FIGS. 2A and 2B** illustrate phase diagrams for alloys that provide the desired properties. In **FIG. 2A**, which reflects, for example, the rhodium-silicon system, there is very limited solid solubility of the alloying element around room temperature. In **FIG. 2B**, which reflects, for example, the rhodium-aluminum, or rhodium-boron system, there is essentially no solid solubility of the alloying element in the rhodium matrix around room temperature and up to several hundred degrees Celsius. As reflected in the phase diagrams, there exist higher tempera-

ture regions where it is possible to decompose a metastable solid solution and therefore form a second phase with moderate heating schemes. Within these temperature regions, the features of the alloys can be easily tailored.

[0027] Several metals with phase diagrams similar to that depicted in FIGS. 2A and 2B exist. The desired solid solubility of alloying elements in the noble metal matrix is less than 4 weight percent, advantageously less than 2 weight percent and more advantageously less than 0.5 weight percent, at or near room temperature (about 25°C.). Typical compositions of the noble metal-based contact alloys contain 0.1-30 weight percent of the alloying element, advantageously 0.5-10 weight percent, and more advantageously 1-5 weight percent, with the particular amount varying depending on, among other things, the particular solubility and the desired degree of alloy strengthening. Control samples are easily prepared to allow one to tailor the properties to a particular application.

[0028] Rhodium-based alloy systems suitable for the wear-resistant contact materials of the invention, in which alloying elements have limited solubility in rhodium, include Rh—C, Rh—Ce, Rh—Dy, Rh—Y, Rh—Si, Rh—Zr, Rhodium-based alloy systems in which the alloying elements have essentially no solubility in rhodium include Rh—Al, Rh—B, Rh—Bi, Rh—Er, Rh—Gd, Rh—Ge, Rh—Pb, Rh—Sm, and Rh—Yb. In these systems, the precipitates formed are typically intermetallic compounds according to the phase diagrams. (See, e.g., *Binary Alloy Phase Diagrams*, 2nd Ed., ASM International (1990).) Alloying systems to be avoided include R—Co, R—Cr, R—Ir, R—Cu, R—Fe, R—Hf, R—Mn, R—Mo, R—Nb, R—Ni, R—Os, R—Pd, R—Ru, R—Sb, R—Sn, R—Ta, R—Ti, R—V, R—W, as these alloying elements have substantial residual solubility in rhodium even after precipitation, and thereby deteriorate the electrical conductivity of the rhodium.

[0029] For gold (Au) based systems, suitable alloying systems with limited solubility include Au—C, Au—Co, Au—Ho, Au—Lu, Au—Th, Au—Mn, Au—Re, Au—Rh, Au—Ru, Au—Sb, Au—Yb, Au—Y. Systems with essentially no solubility include Au—B, Au—Bi, Au—Dy, Au—Er, Au—La, Au—P, Au—Pb, Au—Si, Au—Sr, Au—W. Alloy systems to be avoided include Au—Ag, Au—Al, Au—Fe, Au—In, Au—Li, Au—Mg, Au—Nb, Au—Ni, Au—Pd, Au—Pt, Au—Sn, Au—Ta, Au—Ti, Au—V, Au—Zn, Au—Zr.

[0030] For platinum (Pt) based systems, suitable alloys with limited or no solubility include Pt—B, Pt—Bi, Pt—Er, Pt—Pb, Pt—La, Pt—Mo, Pt—Ti (B and Ti having limited solubility and the others having essentially no solubility). Systems to be avoided include Pt—Al, Pt—Nb, Pt—Ni, Pt—Os, Pt—Mn, Pt—Mo, Pt—V.

[0031] For palladium—based (Pd) systems, suitable alloys include Pd—B, Pd—Bi, Pd—Si (B having limited solubility and the others having essentially no solubility). Systems to be avoided include Pd—Fe, Pd—Al, Pd—C, Pd—Hf, Pd—Mn, Pd—Ir, Pd—Y, Pd—Dy, Pd—Ho, Pd—Ta, Pd—Mo, Pd—Nb, Pd—Ni, Pd—Pb.

[0032] For ruthenium—based (Ru) systems, suitable alloys include Ru—C, Ru—Ce, Ru—Hf, Ru—Lu, Ru—La, Ru—Si, Ru—Bi, Ru—Gd (C, Ce, and Hf having limited

solubility, and the others having essentially no solubility). Systems to be avoided include Ru—Co, Ru—Cr, Ru—Mo, Ru—Ti, Ru—Fe, Ru—Ir, Ru—Nb, Ru—Ni, Ru—Os, Ru—Re.

[0033] When such alloys, for example, Au—B, Rh—Al or Rh—Si, are deposited as a thin film at an ambient or low temperatures, the alloy tends to form as a metastable, supersaturated solid solution, well beyond the thermodynamically-allowed solid solubility limit. Due to this instability, the forced-in alloying element precipitates out whenever thermal movement of atoms is allowed, and the desired alloy decomposition, i.e., precipitation, therefore occurs. It is possible for this decomposition to occur during thin film deposition, e.g., by heating the substrate, or alternatively during a post-deposition heat treatment. The presence of precipitates provides a strengthening mechanism—the precipitates impede the movement of dislocations and grain boundaries, and the alloys are therefore harder than the elemental noble metal itself or solid-solutioned noble metal alloys. The contribution of the precipitates to improving the mechanical strength of the films also improves the wear resistance of the films. An additional advantage of using such a forced-in alloy system is that the noble metal matrix becomes depleted with the alloying element as alloy decomposition occurs. Thus, the electrical conductivity of the alloy improves after such precipitation, to a relatively high value that is often comparable to the conductivity of the noble metal itself.

[0034] In fact, the techniques for providing alloy strengthening and improved wear resistance according to the invention are able to provide a relatively low loss of electrical conductivity, contrary to conventional alloying practices. In particular, the electrical conductivity of the alloy of this embodiment is typically at least 15% of the conductivity of the pure element noble metal, advantageously at least 30% of the conductivity of the pure element, more advantageously at least 50% of the conductivity of the pure element. The mechanical hardness of the alloy should be at least 30% greater than the hardness of the pure element, advantageously at least 50% greater than the hardness of the pure element, more advantageously at least 100% greater than the hardness of the pure element. The hardness of the alloy should be at least 15% greater than the hardness of the same alloy but in single phase form, advantageously 30% greater, and more advantageously at least 60% greater.

[0035] The microstructure of the alloys of this first embodiment contain a fine distribution of precipitate particles, the particles typically less than 500 nm in average diameter, advantageously less than 150 nm, more advantageously less than 50 nm. The precipitate particles are typically present in a volume fraction of 0.1% to 30%, advantageously 0.5% to 5%. (Greater than 30% tends to deteriorate the conductivity and cause embrittlement.)

[0036] This microstructure is generally obtained by one of two processing techniques. The first is to create such a structure in situ by film deposition (e.g., sputtering) with the substrate temperature sufficiently high (typically greater than 100° C., advantageously greater than 200° C.) to drive the segregation of the second phase precipitate during the deposition. In this case, no post-deposition annealing process is needed.

[0037] The second approach is to prepare the thin film with the supersaturated alloying element as a solid solution

in the noble metal matrix, and then, after deposition of the film, perform a post-deposition heat treatment to decompose the alloy and create the desired precipitates. Upon heating, the alloy will be in a two-phase region and precipitates will form. Continuous heating and cooling, or isothermal holding at a constant temperature, are both possible. Typical decomposition temperatures are 100-800° C., advantageously 100-400° C. Typical decomposition time is 0.01-100 hours, advantageously 0.1-20 hours. A schematic illustration of the microstructures of the metal before and after decomposition heat treatment is illustrated in **FIGS. 3A and 3B**. In **FIG. 3A**, the as-deposited (but not heat treated) microstructure **30** contains forced-in solute atoms, but no precipitates. In **FIG. 3B**, the post-heat treatment microstructure **40** contains the desired precipitates **42**. The heat treatment generally improves the electrical conductivity, compared to the as-deposited alloy, by at least 30%, due to movement of solute atoms from the matrix to the precipitates.

[0038] The alloys of this embodiment are formed into thin films appropriate for contacts by any suitable technique, including sputtering, thermal evaporation, electron-beam evaporation, laser ablation, glow discharge, ion plating, ion-beam assisted deposition, ion-cluster beam techniques, chemical vapor deposition, electrolytic deposition, and electroless plating.

[0039] In a second embodiment, the improved contact alloy is a composite structure containing a noble metal or alloy matrix and insoluble, non-coarsening dispersoid particles. The composite structure provides high mechanical strength with substantially no solid-solution-induced loss of electrical conductivity.

[0040] The materials selected for the dispersoids have essentially no solid solubility in the noble metal matrix. **FIG. 4** illustrates a typical microstructure for inventive composite-structured contact metal with desirable microstructural characteristics. The matrix **50** is a noble elemental metal or alloy within which nano-scale, insoluble dispersoid particles **52** are distributed. The dispersoid particles impede the motion of dislocations or grain boundaries, thus increasing the contact metal strength and wear resistance. The insolubility reduces the possibility that the conductivity will be compromised, in contrast to conventional alloying in which the electrical conductivity generally deteriorates due to solute atom additions. The insolubility also reduces the extent to which the second phase (dispersoid particles) can coarsen (grow) during heat treatment, repeated contact operations, local heating, exposure to ambient temperature rise, and similar actions, which is desirable since such coarsening typically causes a deterioration in strength and wear resistance.

[0041] It is possible for the noble metal matrix to be a pure element, an alloy of several noble metal elements, or multilayer thin film structure of such elements. Dispersoid particles include oxides, nitrides, carbides, sulfides, and fluorides, as well as other insoluble stable compounds such as oxynitrides or oxycarbides. Such materials are capable of being produced by reaction of various elements with reactive gases, e.g., oxygen, air, or water in the case of oxides; nitrogen or ammonia in the case of nitrides; methane, acetylene, or propane in the case of carbides; H₂S in the case of sulfides; and HF or CF₄ in the case of fluorides. Particular dispersoid materials include Al₂O₃, SiO₂, TiO₂, ZrO₂, HfO₂,

MgO, Y₂O₃, In₂O₃, SnO₂, GeO₂, Ta₂O₅, AlN, BN, Si₃N₄, TiN, ZrN, TaN, WC, SiC, TaC, TiC, ZrC, CdS, CuS, ZnS, and MgF₂, CaF₂, CeF₃, ThF₄. Oxycarbides and oxynitrides of Ti, Ta, Al, and Si, along with arsenides, amorphous phases, intermetallics, fullerenes, and nanowires (e.g., carbon nanotubes) are also capable of acting as dispersoid material. The dispersoid particles typically range in size from 1 to 5000 nm, advantageously 2 to 500 nm, more advantageously 2 to 50 nm. The dispersoid particles are typically present in the alloy in an amount ranging from 0.1 to 30 volume percent, advantageously 0.5 to 5 volume percent. Too high a volume fraction, for example in excess of 30%, tends to deteriorate the electrical conductivity of the noble metal, and also tend to lead to undesirable embrittlement of the contact material.

[0042] The alloys of this second embodiment are able to be fabricated into a thin film configuration by any suitable technique, e.g. sputtering, thermal evaporation, electron-beam evaporation, laser ablation, glow discharges, ion plating, ion-beam assisted deposition, ion-cluster beam techniques, chemical vapor deposition, electrolytic deposition or electroless plating with simultaneous trapping during deposition of dispersoid particles mixed in the liquid.

[0043] A particularly useful process for preparing the alloy of this second embodiment is co-deposition or co-sputtering from two separate targets—one containing the noble metal matrix material and the other containing the dispersoid material, as illustrated in **FIG. 5**. The Figure shows sputtering, e.g., dc-magnetron sputtering, of a noble metal target **60** and sputtering, e.g., rf-sputtering, of an oxide target **62** being simultaneously performed to obtain a composite structure having dispersoid particles **66** within a noble metal matrix **68**. It is possible for the co-deposition to be carried out on a heated substrate **64**, e.g. heated to a temperature of 50 to 500° C., to accelerate the formation of stable dispersoid compound during the film deposition. Alternatively, it is possible to first form a composite film at room temperature and then perform a post-deposition heat treatment to aid in the formation of stable dispersoid particles of a desired size, e.g., by heating at 100 to 500° C. for 1 to 10,000 minutes. Such post-deposition heat treatment is advantageously carried out either in an inert atmosphere (such as argon, helium or nitrogen), in a reducing atmosphere (such as H₂, H₂+N₂, CO), or in a vacuum, to reduce or avoid oxidation of the contact metal film surface.

[0044] Another technique for forming the alloy of this second embodiment is an in-situ reactive deposition technique, such as reactive sputtering or evaporation in an oxygen-containing atmosphere, as reflected in **FIG. 6**. The sputtering target **70** contains both the noble metal **72** and the reactive dispersoid-forming metal **74**, for example, an Rh-Al alloy target or a target having separate areas of Rh and Al. During deposition, the Al atoms react with oxygen atoms in the atmosphere and form Al₂O₃ particles **76**, which are trapped and incorporated in the unreactive Rh metal film **78** deposited on the substrate **80**. A variety of dispersoid-forming metals are possible, including Al, Ti, Si, Mg, Zr, W, Ta, and Y. These elements are capable of reacting with oxygen, nitrogen or fluorine atoms in a deposition chamber to form the corresponding oxide, nitride or fluoride. It is also possible to vary this technique to deposit films in a oxidizing

plasma, i.e., use an rf-excited discharge and an oxygen pressure of less than one Torr to generate oxide particles within the matrix material.

[0045] Another technique suitable for preparing the composite alloy of this second embodiment is an internal oxidation process. As illustrated in FIG. 7, a pure noble metal or noble metal alloy film 90 containing one or more strongly oxidizing elements such as Al, Ti, Si, Zr, or rare earth elements is deposited onto a substrate 92, with atoms of these oxidizing elements metastably incorporated in the noble metal matrix. The film 90 is then subjected to a heat treatment in a chamber 94 filled with an oxidizing atmosphere such as O₂, O₃ or Ar+O₂, such that sufficient oxygen atoms diffuse into the deposited film 90 to react with the oxidizable element atoms and form oxide dispersoid particles 96.

[0046] The alloys of this second embodiment exhibit a relatively low loss of electrical conductivity, versus the matrix metal alone, while offering improved wear resistance. The conductivity of the alloy is typically at least 50% of the conductivity of the noble metal matrix alone, advantageously at least 80%, more advantageously at least 90%. The mechanical hardness of the alloy is typically at least 30% greater than that of the noble metal matrix alone, advantageously at least 50% greater, more advantageously at least 100% greater.

[0047] The alloys of the invention, when used as contact materials, e.g., in MEMS relays, are typically formed as a film having a thickness of 1 to 10,000 nm, advantageously 1 to 1000 nm. However, noble metals, because of their inert nature, tend to exhibit poor adhesion to substrates, particularly when deposited as a thin film, and often delaminate. To improve the adhesion between the noble metal alloys of the invention and substrate surfaces, e.g., in microrelay devices, it is possible to first deposit one or more adhesion-promoting layers onto the substrate. Useful metals for such adhesion-promoting layers include chromium, titanium, tantalum, zirconium and alloys containing such metals. To provide smooth transition from the adhesion-promoting layer to the contact alloy, it is possible to add a small amount of these adhesion promoting elements to the alloy, e.g., 0.1 to 5 weight percent, advantageously 0.1 to 1 weight percent. The typical thickness of the adhesion-promoting layer is 1 to 1000 nm, advantageously 1 to 100 nm.

[0048] To simplify fabrication of the contacts, it is often desirable to use alloying systems that do not require such adhesion-promoting measures. It is possible to attain both self-adherence and wear resistance by selection of alloying elements. Useful matrix-alloying element combinations for providing these properties include Rh—Si, Rh—Al, R—Zr, R—Y, R—Sm, A—Si, A—Dy, A—La, P—Ti, P—La, P—Si, R—Hf, R—Si, and R—La. It is notable that several of these alloying elements are suitable for forming precipitates according to the first embodiment of the invention, or insoluble dispersoids according to the second embodiment, depending on the formation process. Alloys containing Si are particularly useful for MEMS relay contacts, as the substrate surface in MEMS devices typically are silicon dioxide (SiO₂) or silicon (Si), onto which contact alloys containing silicon bond well.

[0049] Other embodiments of the invention will be apparent to those skilled in the art from consideration of the specification and practice of the invention disclosed herein.

What is claimed is:

1. An article comprising at least one electrical contact formed from an electrically conductive alloy comprising:

one or more noble metal elements;

one or more alloying elements, wherein the solid solubility of each of the one or more alloying elements in each of the one or more noble metal elements is less than 4 weight percent and wherein the one or more alloying elements are present in the alloy in a total amount of 0.1 to 30 weight percent; and

precipitate particles comprising the one or more alloying elements, wherein the particles have an average diameter less than 500 nm, and are present in a volume fraction of 0.1 to 30%,

wherein the mechanical hardness of the alloy is at least 30% greater than the mechanical hardness of the one or more noble metal elements alone.

2. The article of claim 1, wherein the solid solubility of each of the one or more alloying elements is less than 2 weight percent.

3. The article of claim 2, wherein the solid solubility of each of the one or more alloying elements is less than 0.5 weight percent.

4. The article of claim 1, wherein the mechanical hardness is at least 50% greater.

5. The article of claim 1, wherein the one or more noble metal elements is rhodium and the one or more alloying elements are selected from the group consisting of C, Ce, Dy, Y, Si, Zr, Al, B, Bi, Er, Gd, Ge, Pb, Sm, and Yb.

6. The article of claim 1, wherein the one or more noble metal elements is gold, and the one or more alloying elements are selected from the group consisting of C, Co, Ho, Lu, Th, Mn, Re, Rh, Ru, Sb, Yb, Y, B, Bi, Dy, Er, La, P, Pb, Si, Sr, and W.

7. The article of claim 1, wherein the one or more noble metal elements is platinum, and the one or more alloying elements are selected from the group consisting of B, Bi, Er, Pb, La, Mo, and Ti.

8. The article of claim 1, wherein the one or more noble metal elements is palladium, and the one or more alloying elements are selected from the group consisting of B, Bi, and Si.

9. The article of claim 1, wherein the one or more noble metal elements is ruthenium, and the one or more alloying elements are selected from the group consisting of C, Ce, Hf, Lu, La, Si, Bi, and Gd.

10. The article of claim 1, wherein the alloy exhibits an electrical conductivity that is at least 30% of the electrical conductivity of the one or more noble metal elements alone.

11. The article of claim 10, wherein the alloy exhibits an electrical conductivity that is at least 50% of the electrical conductivity of the one or more noble metal elements alone.

12. The article of claim 1, wherein the contact is formed on an adhesion promoting layer that is formed on a substrate

13. The article of claim 1, wherein the alloy comprises Rh and Si, Rh and Al, Rh and Zr, Rh and Y, Rh and Sm, Au and Si, Au and Dy, Au and La, Pt and La, Pd and Si, Ru and Hf, Ru and Si, or Ru and La.

14. The article of claim 1, wherein the article comprises a microrelay device comprising at least two contacts formed from the electrically conductive alloy.

15. The article of claim 14, wherein the microrelay device further comprises a base structure having one of the contacts located thereon and a cantilever structure having another of the contacts located thereon.

16. The article of claim 1, wherein the precipitates are present in a volume fraction of 0.5 to 5%.

17. A process for fabricating an article, comprising the steps of:

providing a substrate; and

depositing on the substrate an alloy comprising one or more noble metal elements, and one or more alloying elements, wherein the solid solubility of each of the one or more alloying elements in each of the one or more noble metal elements is less than 4 weight percent and wherein the one or more alloying elements are present in the alloy in a total amount of 0.1 to 30 weight percent,

wherein the substrate is heated to at least 100° C. during the deposition such that, upon deposition, particles comprising the one or more alloying elements precipitate, the particles having an average diameter less than 500 nm and being present in the alloy in a volume fraction of 0.3 to 30%.

18. The process of claim 17, wherein the alloy comprises Rh and Si, Rh and Al, Rh and Zr, Rh and Y, Rh and Sm, Au and Si, Au and Dy, Au and La, Pt and La, Pd and Si, Ru and Hf, Ru and Si, or Ru and La.

19. A process for fabricating an article, comprising the steps of:

providing a substrate;

depositing on a substrate an alloy comprising one or more noble metal elements, and one or more alloying elements, wherein the solid solubility of each of the one or more alloying elements in each of the one or more noble metal elements is less than 4 weight percent and wherein the one or more alloying elements are present in the alloy in a total amount of 0.1 to 30 weight percent; and

heat treating the deposited alloy at a temperature of at least 100° C. subsequent to deposition, such that particles comprising the one or more alloying elements precipitate, the particles having an average diameter less than 500 nm and being present in the alloy in a volume fraction of 0.3 to 30%.

20. The process of claim 20 wherein the alloy comprises Rh and Si, Rh and Al, Rh and Zr, Rh and Y, Rh and Sm, Au and Si, Au and Dy, Au and La, Pt and La, Pd and Si, Ru and Hf, Ru and Si, or Ru and La.

21. The process of claim 19, wherein the heat treatment increases the electrical conductivity, compared to the electrical conductivity of the deposited alloy, by at least 30%.

22. An article comprising at least one electrical contact formed from an electrically conductive alloy comprising:

one or more noble metal elements; and

one or more types of insoluble dispersoid particles, wherein the insoluble dispersoid particles are present in the alloy in a total amount of 0.1 to 30 weight percent, and wherein the mechanical hardness of the alloy is at least 30% greater than the mechanical hardness of the one or more noble metal elements alone.

23. The article of claim 22, wherein the dispersoid particles range in size from 2 to 500 nm.

24. The article of claim 23, wherein the dispersoid particles range in size from 2 to 50 nm.

25. The article of claim 22, wherein the noble metal elements are selected from the group consisting of gold,

rhodium, platinum, palladium, ruthenium, and silver, and the dispersoid particles are selected from the group consisting of oxides, nitrides, carbides, and fluorides.

26. The article of claim 22, wherein the alloy exhibits an electrical conductivity that is at least 50% of the electrical conductivity of the one or more noble metal elements alone.

27. The article of claim 26, wherein the alloy exhibits an electrical conductivity that is at least 80% of the electrical conductivity of the one or more noble metal elements alone.

28. The article of claim 22, wherein the article comprises a microrelay device comprising at least two contacts formed from the electrically conductive alloy.

29. The article of claim 28, wherein the microrelay device further comprises a base structure having one of the contacts located thereon and a cantilever structure having another of the contacts located thereon.

30. The article of claim 22, wherein the contact is formed on an adhesion promoting layer that is formed on a substrate.

31. A process for forming an article, comprising the step of forming at least one electrical contact from an electrically conductive alloy that comprises one or more noble metal elements and one or more types of insoluble dispersoid particles, the insoluble dispersoid particles being present in the alloy in a total amount of 0.1 to 30 weight percent, and the mechanical hardness of the resultant alloy being at least 30% greater than the mechanical hardness of the one or more noble metal elements alone.

32. The process of claim 31, wherein the step of forming the at least one contact comprises:

providing a substrate; and

forming a film on the substrate by co-sputtering from a first target comprising the one or more noble metal elements and from a second target comprising a dispersoid material insoluble in the one or more noble metal elements.

33. The process of claim 31, wherein the step of forming the at least one contact comprises:

providing a substrate; and

forming a film onto the substrate by sputtering from a target that comprises the one or more noble metal elements and a dispersoid-forming material, wherein the sputtering is performed in an atmosphere comprising one or more gases reactive with the dispersoid-forming elements, such that the insoluble dispersoid particles are formed in the deposited film.

34. The process of claim 33, wherein the atmosphere comprises at least one gas selected from the group consisting of oxygen-containing gases, nitrogen-containing gases, and fluorine-containing gases.

35. The process of claim 31, wherein the step of forming the at least one contact comprises:

providing a substrate;

forming on the substrate a film comprising the one or more noble metal elements and one or more dispersoid-forming elements selected from the group consisting of Al, Ti, Si, Zr, and rare earth elements; and

heat treating the film in an oxidizing atmosphere to induce formation of oxide dispersoid particles from the dispersoid-forming elements.

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