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P. E. DUWEZ
METHOD FOR MAKING A NOVEL SOLID METAL ALLOY
AND PRODUCTS PRODUCED THEREBY

3,297,436

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2 Sheets-Sheet 1

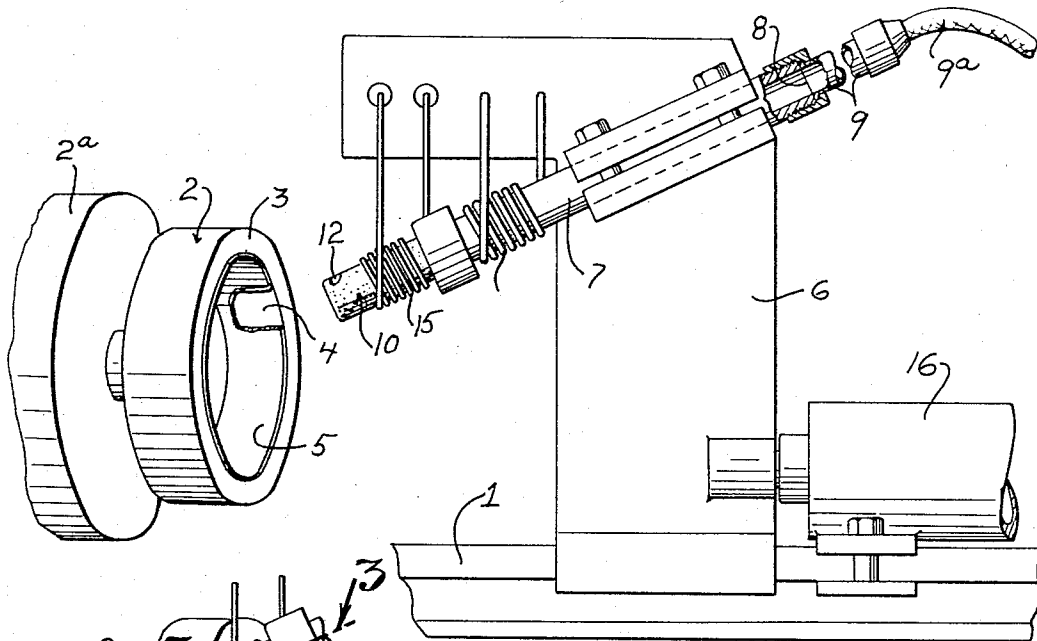


FIG. 1

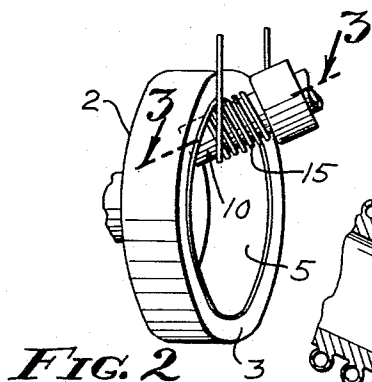


FIG. 2

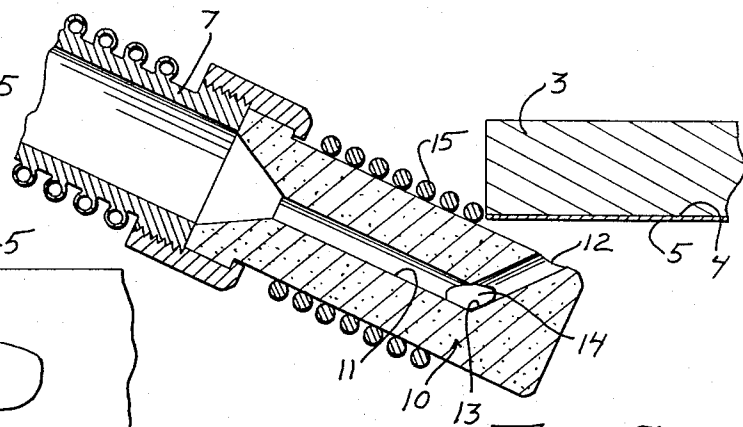


FIG. 3

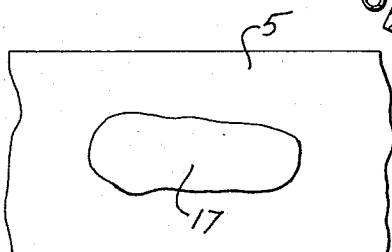


FIG. 4

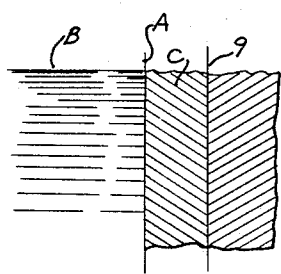


FIG. 5
PRIOR ART

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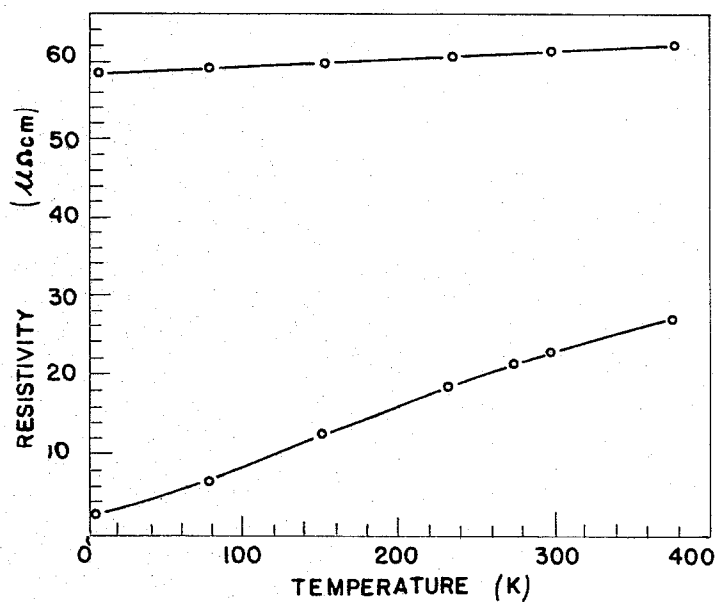


FIG. 6

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METHOD FOR MAKING A NOVEL SOLID METAL ALLOY AND PRODUCTS PRODUCED THEREBY

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10 Claims. (Cl. 75-134)

This invention relates to solid materials and means and methods of producing same and is a continuation-in-part of my co-pending application Serial No. 166,240, filed January 15, 1962, now abandoned, which in turn is a continuation-in-part of an application filed January 15, 1960, Serial No. 3,089, for Solid Material and Means and Method of Producing Same, now abandoned.

When a mixture of metals or salts are cooled from a homogenous melt, the process of solidification involves a relatively gradual flow of heat outwardly from the melt to the walls of the surrounding crucible, mold, or other containing means. During this solidification process, an interface exists between the solidified material and the remaining melt. This interface moves away from the walls of the containing means as solidification progresses. The rate at which the liquid melt goes through the solidification temperature depends on the rate that heat can be extracted from the walls of the container. In the usual process of solidification, this rate is such that the solidification at the interface can take place by nucleation and growth of the various phases of the alloy in the solid state.

If, however, the rate of heat extraction is caused to exceed a critical value for the particular melt, the normal process of nucleation and growth may be prevented; and, as a result, a solid material may be produced having different structural, physical, and mechanical properties from the material obtained as a result of normal cooling.

Accordingly, an object of this invention is to provide a novel, solid material wherein the structure and the distribution of the phases of the solid material are substantially different from the structure obtained when presently known techniques are used to cool a liquid having those phases through the solidification temperature.

Another object of this invention is to provide a means and method wherein heat is extracted from molten material at a rate which substantially prevents the normal process of nucleation and growth of the crystalline phases of the material, thereby to produce a metastable solid material having physical, mechanical, and chemical properties differing substantially from the initial material when cooled in the normal manner.

Yet another object of this invention is to provide a means and method of producing novel, solid materials from a molten mixture by cooling the molten mixture at a rate high enough to substantially overcome the effects of atomic motion whereby nucleation and solid phase growth occurs.

Still another object of the invention is to provide a useful means and method of cooling molten materials at a rate not achievable heretofore.

A still further object of the present invention is to provide amorphous palladium-silicon alloys which have an extremely low temperature coefficient of resistivity and other amorphous silicon alloys having the same property.

These and other objects of the invention are achieved in an arrangement wherein a molten mixture is cooled to a solid at a rate so rapid as to control or even to prevent the process of nucleation and growth of crystalline phases which occur when the presently known methods of cooling a molten mixture are employed. The rapid cooling is achieved by suddenly applying the molten specimen to be

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cooled to a much larger cooling body with a force sufficient to spread the molten specimen into a thin layer and applying sufficient pressure on said molten material to maintain it in intimate contact with the cooling body.

With the above and other objects in view as may appear hereinafter, reference is directed to the accompanying drawings in which:

FIGURE 1 is a fragmentary, substantially diagrammatical view showing one form of an apparatus for effecting rapid cooling of a molten material which utilizes a rotatable drum and a crucible means, the crucible means being disposed in separated relation as they appear during the heating of the material to a molten state;

FIGURE 2 is a similar fragmentary, diagrammatical view thereof, showing particularly the relationship of the rotatable drum and crucible during the step of producing the solid material;

FIGURE 3 is a fragmentary, longitudinal sectional view through the drum, crucible, and adjacent shock tube, taken approximately through 3-3 of FIGURE 2 and viewed from the opposite direction from FIGURE 2;

FIGURE 4 is a fragmentary, substantially diagrammatical view showing the solid material produced, as it appears on the heat-conducting surface of the rotatable drum;

FIGURE 5 is a diagrammatical view showing the manner in which the material is normally cooled from a liquid to a solid state;

FIGURE 6 is a graphic illustration of the temperature coefficients of resistivity of amorphous and crystalline palladium-silicon alloys.

When a mixture of metals or salts are cooled from a homogenous melt, solidification occurs at a rate determined by the rate of heat transfer through the walls of the crucible, mold, or other container for the melt. With reference to FIGURE 5, during the solidification process, an interface A exists between the molten material B and the solid material C. The interface moves away from the surrounding walls D to the center of the material B. Even though a container may be selected so as to have a high rate of heat adsorption by use of cooling jackets, or the like, still the rate of solidification is so slow that nucleation and grain growth readily occur so that the solid product does not have the randomly dispersed atoms as exist in the material when in the molten state.

Even if attempts are made to drop small quantities of material into a cold liquid, the rate of heat transfer is not sufficient to "trap" the atoms or molecules, either at the same locations as they occupy in the molten state or at locations intermediate to the complete randomness which exists in the molten state and the equilibrium positions existing in the solid material when cooled under normal conditions.

In the exercise of the present invention, the molten material is subjected to three conditions:

(1) The molten material is suddenly placed and maintained in contact with a good heat conductor.

(2) The contact is made as intimate as possible by exertion of pressure between the molten material and the heat conductor.

(3) The molten material is spread over the heat conductor in such a manner that the molten material during solidification is inherently thin, that is, not greater than one thousandths of a millimeter (.001 mm.), so that only a small amount of heat need be removed from each unit area to cause a sufficiently rapid cooling.

Reference is directed to FIGURES 1, 2 and 3.

The apparatus here shown may be mounted on a bed 1 and includes a motor 2a which drives a rotatable drum 2 having a cylindrical rim 3. The rim 3 provides an internal cylindrical surface 4 against which molten ma-

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terial may be projected. If desired, a removable liner 5 in good thermal contact with the surface 4 may be used. The rim 3 and liner 5, if used, are preferably formed of a good heat-conducting material, such as copper, silver, gold, platinum, or the like.

Slidably mounted on the bed 1 is apparatus for projecting a charge of molten material against the internal cylindrical surface of the drum. This is shown by way of illustration and should not be considered as a limitation on the invention since other suitable ways of projecting a charge of molten material against the drum surface are known and may be used. The charge-projecting apparatus includes a carriage 6 which supports a shock tube 7, at one end of which is provided a rupturable diaphragm valve 8 separating the shock tube 7 from a pressure tube 9 connected to a source of pressure through a flexible line 9a. The other end of the shock tube is connected to a crucible 10 having a small longitudinal bore 11 and a nozzle 12 intersecting the bore at an obtuse angle to form a pocket 13 adapted to receive a small charge of material 14 which is to be melted. The crucible 10 is surrounded by a heating coil 15. To prevent conduction of excessive heat to the shock tube 7, a coolant coil may surround the end of the shock tube adjacent to the crucible.

The method of producing a solid material utilizing the above-described apparatus is as follows:

A charge of material 14 is placed in the pocket 13 and heated to above its melting point. The drum 2 is rotated, preferably at high speed, so that any material on its internal surface 4 or liner 5 would be subjected to high centrifugal force, preferably a centrifugal force corresponding to several thousand times that of gravity.

In addition, the drum 2 and liner 5 may be chilled by conventional refrigerating equipment, or by liquid nitrogen, helium or the like.

Also a gas, preferably a light gas such as helium, is introduced into the pressure tube 9 to a point just below the rupturing pressures of the diaphragm valve 8.

The carriage 6 is then moved along the bed 1, by any suitable means such as a power cylinder 16, to bring the nozzle 12 of the crucible 10 into substantially tangential relation with the internal surface 4 or liner 5. The pressure in the pressure tube 9 is then raised above the rupturing pressure of the diaphragm valve 8. Upon rupturing of the diaphragm valve, the molten charge of material 14 is driven at high velocity against the internal surface 4 or liner 5 at an obtuse angle.

The angle of impact and the velocity are such as to avoid any appreciable penetration into the surface. That is, the molten charge is not driven at such high velocity as to act as a projectile. As a consequence, the molten material is instantly flattened to form an irregular spot 17 of material as represented in FIGURE 4. By reason of the centrifugal force exerted on the material, intimate contact without the formation of a vapor layer between the material and the surface 4 or liner 5 not only initially is accomplished but also is maintained until the drum is stopped and the material is scraped or otherwise forced free of the surface.

Also by reason of the velocity by which the material strikes the internal surface 4, the material is quite thin (less than one thousandth of a millimeter .001 mm.) and the area of contact is so great that the heat is extracted with such rapidity that the normal process of nucleation and grain growth and for phase formation cannot occur.

In a particular experiment a charge was formulated formed of silver and copper and weighing approximately 25 milligrams. The charge was heated in the crucible above its melting temperature. The internal surface of the drum was rotating at a speed of approximately 400 feet per second. The pressure in the driving gas chamber or pressure tube 9 was in the range of 800 pounds per square inch. The distance between the nozzle and the target, that is, the internal drum surface 4, was ap-

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proximately one-fourth inch. Under these conditions the velocity at which the liquid droplet was discharged was estimated to be about 1000 feet per second at the time it struck the target or internal surface 4. The centrifugal force acting on the liquid layer at the instance of impact was about 6,000 times that of gravity.

It is well known that silver and copper, both being in the liquid state, are completely miscible. A eutectic exists at 60.1 at. percent Ag and there is a limited solid solubility range at both ends of the phase diagram. Four silver-copper alloys containing, respectively, 23.0, 39.9 (eutectic composition), 62.9 and 88.5 at. percent copper were treated by the above described method. Conventionally, such alloys would normally solidify into two different phases, one rich in copper having a maximum of 4.9 at. percent silver, and one rich in silver having a maximum of 14.1 at. percent copper. These conventionally solid alloys consists, therefore, of a mixture of two separate constituents, easily identifiable by X-ray diffraction techniques, or microscopy. When alloys having the above described composition are solidified by the method of the present invention and subjected to X-ray diffraction, the pattern in all cases showed a single phase. On a plot of unit cell size vs. concentration, the lattice parameters obtained with the four metastable alloys fell on a smooth curve connecting the two previously known segments of curves within the solubility limits at both ends of the phase diagram, i.e., 14.1 and 95.1 at. percent Cu.

These results established without doubt that during solidification the two stable phases did not have time to nucleate and grow, and metastable solid solutions were obtained.

The solid solution contained atoms of silver and copper distributed at random in a face-centered cubic lattice. Tests of these alloys demonstrated that the rapid cooling had significantly modified the physical properties of the alloy, including their electrical and mechanical characteristics.

Similarly, silver-germanium alloys having characteristics not before observed may be obtained by this rapid cooling process. Silver and germanium are also miscible in the liquid state and the Ag-Ge equilibrium phase diagram is of the eutectic type with a maximum solubility of germanium in silver at 9.6 at. percent and negligible solubility of silver and germanium. The eutectic composition is at 25.9 at. percent Ge. A silver-germanium alloy containing 25.7 at. percent Ge was formed by the above described method. The resulting solid had a crystal structure that was neither face-centered cubic nor diamond cubic, but rather hexagonal close packed. The presence of a small amount of a diamond cubic Ge phase was indicated by a few weak diffraction peaks on the X-ray pattern.

The new metastable hexagonal phase is believed to be a novel electron compound corresponding to Ag_3Ge .

Yet another novel solid material was made from a molten mixture of gold and silicon using the method and means described. The supercooling technique as taught herein yield a noncrystalline mixture of the constituents very similar to that of glassy materials. Thus, the process of nucleation and growth of crystalline phases was actually prevented.

Depending upon the particular alloys subjected to the rapid cooling of the present invention, three separate types of structures have been observed, (1) the simple cubic lattice, (2) the noncrystalline amorphous solid solutions, and (3) a new crystalline structure which is neither an amorphous nor simple crystalline lattice but rather a complex crystal differing from previously observed crystalline structures. For example, tellurium alloys containing from 10 to 25% silver or from 10 to 65% gold, form a novel tellurium alloy crystallization structure wherein the atoms are distributed at random in a simple cubic lattice.

Tellurium alloys having from 5 to 30% of any one of silicon, germanium, tin, aluminum or gallium, and gold alloys containing from 5 to 8% silicon, may be formed and these alloys are in the form of a noncrystalline amorphous solid solution.

Finally, when gold is alloyed with silver, germanium, thallium or cobalt, or silver is alloyed with germanium or silicon within the percentage ranges dictated by the phase diagrams for these alloys, and are subjected to the cooling process of the present invention, the new crystalline structure is formed.

In each case thin films comparable in thickness to those obtainable by vapor deposit process, may be obtained. In the vapor deposit processes, film thicknesses of from 500 to 2000 Å. are obtained while the films obtained by the above described method range from 500 to 100,000 Å. Further, the films obtained by this process may be removed from the cooling cylinder and utilized in lieu of metallic films formed by vapor processes.

It will be observed that virtually all the known mixtures of metals as well as combinations of many other materials may be subjected to the method hereinbefore described. That is, most combinations of metals or other materials which may be heated to a molten state, then subjected to the rapid cooling as herein set forth, may be utilized. It follows, of course, that with regard to the many such combinations of materials that resulting product will exhibit useful properties and in some instances remarkably new or superior properties.

For example, but by no means representative of the range of unique or improved properties, the resulting product may have:

(a) Improved corrosion resistance as compared to the original composition.

(b) Improved mechanical strength, as much as a factor of 10 as compared to conventional compositions or alloys.

(c) Improved electronic characteristics, as in the field of semi-conductors, the band gap may be controlled or increased as compared to conventional semi-conductors.

(d) Altered electrical resistance, the resistance in general being increased as compared to the conventional alloys or compositions.

(e) Improved magnetic properties, that is, higher coercive force as compared to the conventional alloys or compositions.

By rapid cooling of the melt as by the process described above, amorphous palladium-silicon alloys containing 15-23 at. percent Si may be obtained. Such alloys are stable at room temperature and crystallization cannot be detected after one month at 250° C. At high rates of heating, e.g., greater than 20° C./min., rapid crystallization takes place at 400° C., with a heat release of approximately 1000 cal./mole. These amorphous alloys exhibit a remarkably low temperature coefficient of resistivity as shown in FIGURE 6 where the coefficients of amorphous and crystalline palladium-silicon alloys each containing 17 at. percent Si are compared. As shown in FIGURE 6, the resistivity of the amorphous alloy is about 95% of the room temperature value at 2° K. The coefficient between 2° K. and 300° K. of the alloy is 0.00017/°C. Evidently the electrical conductivity is primarily governed by polyvalent scattering with phonon scattering contributing very little.

The amorphous palladium-silicon alloys of the present invention may be prepared by first melting the components in a fused silica crucible under an argon atmosphere in the above mentioned proportions, e.g., 17 at. percent Si. A very exothermic reaction takes place, probably due to the formation of the compound Pd₂Si, before the melting point of silicon is reached. The molten mass did not wet the crucible and was free from contamination. Rapid cooling from the molten state was achieved according to the process of the present invention described above, but it is to be understood that other procedures could be employed, e.g., that of Pietrokowsky

reported in J. Scientific Instruments 34, 445-446 (1963).

The amorphous structure of the resulting alloy was established by X-ray diffraction, electron diffraction and microscopy. As shown in FIGURE 6, the room temperature resistivity of the resulting alloy is about 2.6 times greater than that of the corresponding crystalline alloy and is uniquely independent of temperature changes. It is this low temperature coefficient of resistivity which makes the amorphous palladium-silicon alloys of the present invention particularly advantageous for use in electrical equipment which will be exposed to widely varying temperatures.

For example, conductors and other elements in the highly sensitive electrical instruments in space vehicles fabricated from these alloys will not require heavy insulation to protect them from the vast temperature changes which occur in the hard vacuum of space and/or will provide added protection against the failure of such insulation.

Having thus described certain embodiments and applications of my invention, I do not desire to be limited thereto, but intend to claim all novelty inherent in the appended claims.

I claim:

1. A novel metastable solid metal alloy film which has not undergone the normal process of nucleation and growth of equilibrium phases prepared by the steps of commingling the constituents of said alloy film, heating said constituents to a molten state under high pressure, forcibly impinging the pressurized molten constituents upon the interior of a rotating chilled cylindrical surface, permitting said molten constituents to be instantly flattened to a thickness of less than 100,000 Angstroms on said surface by centrifugal force and adhering to said cylindrical surface, to form an intimately contacted film thereon, extracting heat from said constituents to said surface to yield a novel metastable solid alloy film, and subsequently stopping said rotating surface and removing said novel cooled alloy film from said surface.

2. A method for producing a novel metastable solid amorphous metal alloy film comprising the steps of commingling the constituents of said alloy film, heating said constituents to a molten state under high pressure, forcibly impinging the pressurized molten constituents upon the interior of a rotating chilled cylindrical surface, permitting said molten constituents to be instantly flattened to a thickness of less than 100,000 Angstroms on said surface by centrifugal force and adhering to said cylindrical surface, to form an intimately contacted film thereon, extracting heat from said constituents to said surface to yield a novel metastable solid alloy film, and subsequently stopping said rotating surface and removing said cooled alloy film from said surface.

3. A method for producing a novel metastable solid metal alloy film comprising the steps of commingling the constituents of said alloy film, heating said constituents to a molten state under high pressure, forcibly impinging the pressurized molten constituents upon the interior of a rotating chilled cylindrical surface, permitting said molten constituents to be instantly flattened to a thickness of less than 100,000 Angstroms on said surface by centrifugal force and adhering to said cylindrical surface, to form an intimately contacted film thereon, extracting heat from said constituents to said surface to yield a novel metastable solid alloy film, and subsequently stopping said rotating surface and removing said cooled alloy film from said surface.

4. The process of claim 3 wherein the alloy is a homogeneous mixture of silver and a metal selected from the group consisting of germanium and silicon.

5. The process of claim 3 wherein said alloy is a mixture of gold and a metal selected from the group consisting of silver, germanium, thallium and cobalt.

6. The process of claim 3 wherein said alloy is a

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homogeneous mixture of about 92-95% gold and 5-8% silicon.

7. The process of claim 3 wherein said alloy is a homogeneous mixture of about 70-95% tellurium and an element selected from the group consisting of silicon, germanium, tin, aluminum and gallium, said selected metal being present in an amount from about 5% to 30%.

8. The process of claim 3 wherein said alloy is a homogeneous mixture of silver and copper.

9. The process of claim 3 wherein said alloy is a homogeneous mixture of tellurium and from about 10 to 65% gold.

10. The process of claim 3 wherein said alloy is a homogeneous mixture of tellurium and from about 10 to about 25% silver.

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