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(54) **ALLIAGES DE ZINC AMELIORES CONTENANT DU TITANE**  
(54) **IMPROVED ZINC BASE ALLOYS CONTAINING TITANIUM**

(57) L'invention découle de la découverte que l'addition de titane à un alliage de zinc contenant la phase epsilon comme phase primaire entraîne une augmentation de la résistance à la traction et de la résistance à la compression de l'alliage. L'alliage peut être utilisé dans les procédés de moulage par gravité, de moulage en coquille ou de moulage sous pression pour produire des pièces ou des outils. Dans la réalisation préférée de cette invention, on ajoute 0,01-0,1 pour cent en poids de titane à un alliage de zinc composé de 3-12 pour cent en poids de cuivre, de 2-5 pour cent en poids d'aluminium et de constituants secondaires, le reste étant constitué de zinc. Ce comportement inattendu n'avait pas été signalé auparavant. La cause de ce comportement est inconnu.

(57) The invention includes the discovery that the addition of titanium to a zinc based alloy containing epsilon as a primary phase results in an increase in tensile and compressive strength of the alloy. The alloy can be used in gravity, permanent mold or die casting processes to mold components or tooling. In a preferred embodiment, 0.01-0.1 weight percent titanium is added to a zinc based alloy containing 3-12 weight percent copper, 2-5 weight percent aluminum, minor constituents and the balance zinc. The discovered behavior was unexpected and has not previously been reported. The cause of such behavior is unknown.

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IMPROVED ZINC BASE ALLOYS CONTAINING TITANIUM

ABSTRACT OF THE DISCLOSURE

The invention includes the discovery that the addition of titanium to a zinc based alloy containing epsilon as a primary phase results in an increase in tensile and compressive strength of the alloy. The alloy can be  
5 used in gravity, permanent mold or die casting processes to mold components or tooling. In a preferred embodiment, 0.01-0.1 weight percent titanium is added to a zinc based alloy containing 3-12 weight percent copper, 2-5 weight percent aluminum, minor constituents and the balance zinc. The discovered behavior was unexpected and has not previously been reported. The cause of  
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## IMPROVED ZINC BASE ALLOYS CONTAINING TITANIUM

### TECHNICAL FIELD

This invention relates to an improvement to zinc based alloys.

### BACKGROUND OF THE INVENTION

5                   Zinc alloys have been used in a variety of applications for decades. Alloys such as Zamak 3 and Zamak 5 were developed in the 1920's to meet the demands for net shape die castings. Subsequently two other alloys, Zamak 2 which is also used in the die casting process, and Kirksite used for making prototype tools and gravity cast process, were developed and  
10 used extensively for this purpose. These alloys contain about 4 weight percent aluminum with a trace of copper in Zamak 3, about 1 weight percent copper in Zamak 5, and about 3 weight percent copper in Zamak 2 and Kirksite. Solidification of these alloys begins with the formation of primary  $\eta$  phase dendrites which are then surrounded by the  $(\eta + \alpha)$  eutectic. The  $\eta$   
15 phase has a hexagonal close-packed (HCP) crystal structure while alpha is face-centered cubic (FCC).

The next significant development in zinc alloys occurred about 25 years ago when a family of Zn-Al alloys, called ZA-5, ZA-8, ZA-12 and ZA-27 were developed; the 5, 8, 12, and 27 indicate the nominal weight  
20 percent aluminum. Solidification of these alloys begins with the formation of primary  $\alpha$  phase dendrites which are then surrounded by the  $(\eta + \alpha)$  eutectic. In all these alloys, aluminum is thought to be the primary strengthening agent. Such alloys can be cast or fabricated in a variety of casting methods with close dimensional tolerances and at a relatively low cost. The typical casting  
25 methods are gravity and pressure die casting processes. Molten zinc alloys

are poured into a fixed volume cavity without pressure (gravity casting) or under pressure as in die casting process.

Commercial zinc die cast alloys, Zamak and Zn-Al (ZA) alloys, are used mainly for decorative or non-structural applications, because of their lower strength and/or creep properties. Stronger materials like steel are used to meet higher requirements. Steel parts are usually machined, whereas, zinc alloys can be die cast to shape. Other zinc alloys like Kirksite (4 weight percent Al, 3 weight percent Cu, balance zinc) are routinely used for prototype tooling for sheet metal stampings. However, Kirksite tooling is relatively soft, and generally unsuitable for high volume production.

Recently developed zinc-base alloys known as ACuZinc® (2-4 weight percent Al, 4-11 weight percent Cu, balance zinc) can be used as a creep resistant zinc alloy, as disclosed in Rashid and Hanna, U.S. Patent No. 4,990,310. These alloys contain  $\epsilon$  dendrites which were surrounded by the ( $\eta + \alpha + \epsilon$ ) ternary eutectic and some  $\eta$  phase. The volume fraction and the size of the  $\epsilon$  phase dendrites increases with copper content. These alloys were found to be stronger and more durable than existing commercial alloys. Recently, these alloys were also found to increase their strength when the strain rate increases and that increases higher at higher temperature. The present invention is a further improvement in the ACuZinc® alloy.

#### SUMMARY OF THE INVENTION

The invention includes the discovery that the addition of titanium to a zinc based alloy containing epsilon as a primary phase results in an increase in tensile and compressive strength of the alloy. The alloy can be used in gravity, permanent mold or die casting processes to mold components or tooling. In a preferred embodiment, about 0.01-0.1 weight percent titanium is added to a zinc based alloy containing about 3-12 weight percent copper, about 2-5 weight percent aluminum, minor constituents and the

balance zinc. The discovered behavior was unexpected and has not previously been reported. The cause of such behavior is unknown.

The addition of titanium improved the toughness of the zinc based alloy. A new Al-Zn-Ti phase ( $Al_5Ti_{10}Zn_3$ ) was formed which acted as a nuclei for the formation of a greater number of finer  $\epsilon$  phases ( $Zn_4Cu$ ) with greater surface area compared to an Zn-Cu-Al alloy without titanium. The greater number and increase surface area of the harder  $\epsilon$  phase improved the toughness of the alloy.

As a result of the increase in compressive strength and toughness with the addition of titanium, these zinc alloys can be used with confidence for automotive and nonautomotive components or tools where such behavior is beneficial. The alloy of this invention can be used in cast-to-size dies for forming sheet metals, a variety of forming and impact tools, components which are subjected to compressive strength and any other parts which must withstand high forces. Alloy components of this invention can be manufactured to shape or near-net shape by die casting or gravity casting.

These and other objects, features and advantages of the present invention will become apparent from the following brief description of the drawings, detailed description and appended claims and drawings.

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#### BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a graphical representation of the effect of titanium addition on room temperature Ultimate Tensile Strength (UTS) and 0.2 percent Yield Strength (0.2% YS) for zinc alloy containing 10.4 weight percent copper, 4.1 percent aluminum and 0.05 percent magnesium.

Figure 2 is a graphical representation of the effect of titanium addition on room temperature tensile elongation of zinc alloy containing 10.4 weight percent copper, 4.1 percent aluminum and 0.05 percent magnesium.

Figures 3A-C are graphical representations of the effect of titanium concentration on the proportional limit on zinc alloy containing 10.4

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weight percent copper, 4.1 weight percent aluminum and 0.05 percent magnesium for: (a) as-cast; (b) aged at 100°C for 10 days; (c) aged at 200°C for 10 days, respectively.

Figure 4A are comparative micrographs showing the effect of titanium concentration on microstructure of zinc alloy containing 10.4 weight percent copper, 4.1 percent aluminum and 0.05 percent magnesium for: (a) as-cast microstructure without the addition of titanium, showing a large primary  $\epsilon$  ( $Zn_4Cu$ ) phase (white dendrites), small amount of  $\eta$  phase as a product of the binary peritectic reaction and the ternary eutectic ( $\eta + \alpha + \epsilon$ ); versus (b) as-cast microstructure with the addition of 0.015 weight percent titanium, showing marked grain refinement of the primary  $\epsilon$  ( $Zn_4Cu$ ) phase, which is the hard phase in alloy.

Figure 4B is a graph of an energy dispersive x-ray analysis of the particles based on  $Al_5Ti_{10}Zn_3$  in the zinc alloy containing 0.015 weight percent titanium according to the present invention, and an enlargement of the micrograph of Figure 4A for the 0.015 weight percent titanium alloy with an  $\epsilon$ -phase and identified as  $Al_5Ti_{10}Zn_3$  as indicated in the x-ray graph.

Figure 5 is a cross sectional view of a cold chamber die casting machine for casting a zinc-aluminum-copper-titanium alloy according to the present invention.

Figure 6 is a cross sectional view of a hot chamber die casting machine for casting a zinc-aluminum-copper-titanium alloy according to the present invention.

## DESCRIPTION OF THE PREFERRED EMBODIMENT

Suitable zinc alloys for the practice of this invention contain titanium in amounts between 0.01 and 0.1 weight percent, copper in amounts between about 3 and 12 weight percent, aluminum in an amount between about 2 and 5 weight percent, magnesium in an amount between 0 and 0.05 weight percent and the balance substantially zinc, plus iron and other typical

impurities. For hot chamber die casting, the preferred copper content is between about 5 and 7 weight percent. Alloys containing less than 4 percent copper fail to form significant epsilon phase, whereas greater than about 8 percent copper results in an elevated melting point impractical for typical hot chamber die casting apparatus. In contrast, a preferred copper range for cold chamber alloy is between about 9 and 11 weight percent. Above about 12 weight percent copper, the formation of additional phases interfere with the desired epsilon-eta-eutectic microstructure.

A preferred aluminum range for alloys in the practice of the present invention is between about 2 and 5 weight percent. At least about 2 percent aluminum is desired to provide sufficient fluidity for convenient handling at common die casting temperature. Alloys having substantially greater than about 4 percent aluminum develop unwanted alpha phase.

A minor presence of magnesium is desired to improve dimensional accuracy and reduce stress corrosion cracking. A preferred magnesium range is between about 0.025 and 0.05 weight percent.

The following is a description of a working example and result for an alloy according to the present invention. The base metal selected for this example was commercial purity zinc alloy containing 10.4 weight percent copper, 4.1 weight percent aluminum and 0.05 weight percent magnesium. The alloy was melted in a coreless induction furnace and cast into sand tensile molds for tensile applications. Appropriate amount of Al-5 weight percent titanium-1 weight percent boron were added to the molten metal as a master alloy and held for thirty minutes at 650°C, i.e., about 100°C above the liquids temperature and cast into molds for tension and compression specimen.

Tensile specimens (50.8 mm gauge length and 12.9 mm diameter) and compression specimens (50 mm gauge length and 18 mm diameter) were tested in an Instron Universal test machine equipped with a box furnace. Tension tests were conducted on as-cast specimens at room temperature. Compression tests were carried out on both as-cast specimens

and specimens aged in a constant temperature oil bath at 100°C or 200°C for 10 days. The tests were conducted at room temperature, 93°C (200°F), 150°C (300°F), and 177°C (350°F). Specimen temperature was monitored continuously with a thermocouple attached to the specimen surface. The specimens were compressed at a cross head speed of 2.5 mm/min. Load-elongation data was recorded automatically during the test. The proportional limit, or the stress for measurable plastic flow to occur, and the 0.5 percent and 1 percent yield stress values were determined from these data.

Upon the addition of titanium to the zinc alloy containing 10.4 weight percent copper, 4.1 weight percent aluminum and 0.05 weight percent magnesium an increase was observed in tensile properties. The ultimate tensile strength (UTS) with no titanium addition was 301 MPa. Upon the addition of 0.01 to 0.1 percent titanium, the UTS ranged between 342 MPa and 353 MPa, an increase of 13-17 percent (Figure 1). Yield strength changed very slightly. Most of the increase occurs with 0.01 percent titanium. Contrary to conventional wisdom, ductility increased with an increase in UTS. Plastic strain increased from 0.22 percent with no titanium additions to about 0.5 percent for titanium additions of 0.01 to 0.1 percent (Figure 2).

The proportional limit is a measure of initiation of deformation and gives a measure of the strength of the material. The proportional limit during compression, as a function of titanium concentration, is plotted in Figure 3. At room temperature, for both types of specimens (as-cast and aged condition), the proportional limit increased by approximately 20 MPa for titanium additions up to 0.015 percent. Increasing titanium further reversed the trend and tended to decrease the proportional limit. This decrease was more pronounced in the as-cast material than those aged at higher temperatures. Figure 3B shows the trend for specimens aged at 100°C for 10 days and Figure 3C shows the trend for specimens aged at 200°C for 10 days.

In hot compression at 93°C, 150°C, 177°C, the effect of titanium was different than at room temperature. Upon addition of 0.015 weight percent titanium the proportional limit of the zinc alloy decreased by 20-25 MPa depending on the specimen history (aging temperature and time).

- 5 Increasing the titanium concentration for both types of the specimens reversed the trend of decreasing the strength with addition of 0.015 weight percent titanium to about the same level of the strength without titanium addition.

The as-cast microstructure (Figure 4A) of zinc alloy containing 10.4 weight percent copper, 4.1 weight percent aluminum and 0.05 weight  
10 percent magnesium consists of large primary  $\epsilon$  ( $Zn_4Cu$ ) phase (white dendrites), small amounts of  $\eta$  phase as a product of the binary peritectic reaction and the ternary eutectic ( $\eta + \alpha + \epsilon$ ), which precipitate in the final stage of solidification at 378°C. A marked grain refinement was observed in the microstructure by the addition of titanium. With the addition of titanium  
15 and as shown in Figure 4A, the primary crystals of  $\epsilon$  phase (white) which is the hard phase in alloy appeared to be finer and “non-dendritic.” Figure 4B shows that the  $\epsilon$  phase appeared to center on an intermetallic compound, which was identified by energy dispersive x-ray analysis to be based on  $Al_5Ti_{10}Zn_3$  particles, and was probably formed from  $Al_3Ti$  which acted as a  
20 nuclei for the heterogeneous crystallization.

The above results are believed to be the first reported on the new phase. The presence of small grain size per se could not be the only cause for improving the properties. The evidence points also to the peritectic reaction as the additional cause of improving and increasing the strength. The  
25  $\epsilon$  phase which nucleates first, reacts with the liquid and become sheathed with a solid  $\eta$  phase (gray). The higher volume fraction of the  $\eta$  phase observed in the refined alloy is due to larger volume fraction of the surface area of epsilon phase available for peritectic transformation to take place. While there is evidence of grain refinement of the epsilon phase, a detailed understanding of  
30 the actual mechanism for strengthening remains uncertain.

The effect of titanium addition on the room temperature mechanical properties of the as-cast alloy containing 10.4 weight percent copper, 4.1 weight percent aluminum and 0.05 percent magnesium appeared to reach its maximum at 0.015 weight percent titanium, a UTS of 350 MPa, proportional limit on compression of 255 MPa. The aged titanium-containing alloys appear to behave in a similar manner. This behavior expected to have similar effect on all zinc alloys which contain epsilon as a primary phase referenced as ACuZinc® 5 and ACuZinc® 10 and manufactured by gravity, permanent mold or die casting processes. This information combined with the knowledge that the titanium containing material in the range of up to 0.1 weight percent is more dimensionally stable during aging at difference temperatures than the alloy without titanium addition suggest that the titanium containing alloy is preferred for cast-to-size dies which work at room temperature.

A die casting according to the present invention formed of a zinc-base, copper-aluminum-titanium alloy using a conventional cold chamber die casting machine shown schematically in Figure 5. The machine may include a movable platen 11 and a stationary platen 13. Die halves 12 and 14 are mounted on platens 11 and 13, respectively, and cooled by water circulated through passages (not shown) therein. In the closed position shown in the figure, die halves 12 and 14 cooperate to define a fixed-volume die cavity 16 suitably sized and shaped for producing a casting of a desired configuration. At appropriate times during the casting cycle, platen 11 moves relative to platen 13 to part die halves 12 and 14 along a plane indicated by line 18 for ejection of a product casting. Machine 10 also includes a shot apparatus 20 comprising a generally cylindrical shot sleeve 22 that communicates with cavity 16. Sleeve 22 includes an inlet 24 for admitting a molten metal charge 26 poured, for example, from a suitable ladle 28. A hydraulically driven shot plunger 30 is slidably received in sleeve 22 and

advances toward the die sections for forcing metal from sleeve 22 into cavity 16.

Zinc die castings of this invention were also manufactured using a hot chamber die casting machine 50 shown schematically in Figure 4. Machine 50 comprises water-cooled die halves 52 and 54 mounted on a stationary platen 53 and a movable platen 55, respectively, adapted for moving die halves between a closed position shown in Figure 4 wherein the die halves cooperate to form a casting cavity 56 and an open position wherein the die halves are parted along a plane indicated by line 58 for ejection of a product casting. In accordance with common hot chamber die casting process, die casting machine 50 comprises a shot apparatus 60 formed of a goose neck sleeve 62 partially submerged in a molten metal bath 64 contained in melting pot 63. Shot apparatus 60 further comprises hydraulically driven plunger 68 slidably received in goose neck 62. When plunger 68 is in a retracted position shown in the figure, a charge of molten metal from bath 64 fills goose neck 62 through an inlet port 66. For casting, plunger 68 is driven downwardly to force molten metal through sleeve 62 into die cavity 56.

## CLAIMS

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. An alloy comprising about 0.01 to about 0.1 weight percent titanium, about 3 to about 12 weight percent copper, about 2 to about 5 weight percent aluminum, about 81 to about 95 weight percent zinc.

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2. An alloy as set forth in claim 1 including a primary  $\epsilon$  phase, an  $\eta$  phase and an  $\eta + \alpha + \epsilon$  ternary eutectic.

3. An alloy as set forth in claim 1 having between 4 and 7 weight percent copper, and wherein said alloy has been die casted in a hot chamber die casting process.

4. An alloy as set forth in claim 1 having between 7 and 11 percent copper, and wherein said alloy has been die casted in a cold chamber die casting process.

5. An alloy as set forth in claim 1 having titanium in about 0.01 to 0.015 weight percent.

6. An alloy as set forth in claim 1 further comprising minor constituents.

7. An alloy comprising a  $\text{Al}_5\text{Ti}_{10}\text{Zn}_3$  particles.
8. A die casting comprising about 0.01 to about 0.1 weight percent titanium, about 3 to about 12 weight percent copper, about 2 to about 5 weight percent aluminum, about 81 to about 95 weight percent zinc.
9. An alloy as set forth in claim 8 including a primary  $\epsilon$  phase, an  $\eta$  phase and an  $\eta + \alpha + \epsilon$  ternary eutectic.
10. In a zinc-copper-aluminum based alloy, a sufficient amount of titanium to improve the tensile strength of the alloy.
11. An alloy as set forth in claim 10 comprising about 3 to 12 weight percent copper, about 2 to about 5 weight percent aluminum and about 81 to 95 weight percent zinc.
12. In a zinc-copper-aluminum based alloy, a sufficient amount of titanium to increase the surface area of an  $\epsilon$  phase compared to an alloy without the titanium.
13. An alloy as set forth in claim 12 comprising about 3 to 12 weight percent copper, about 2 to about 5 weight percent aluminum and about 81 to 95 weight percent zinc.

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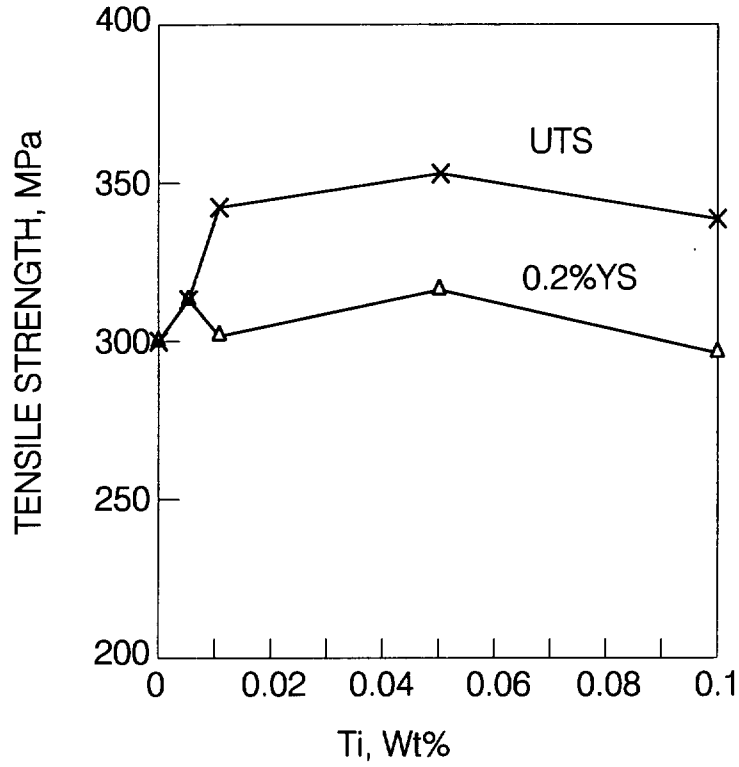


FIG. 1

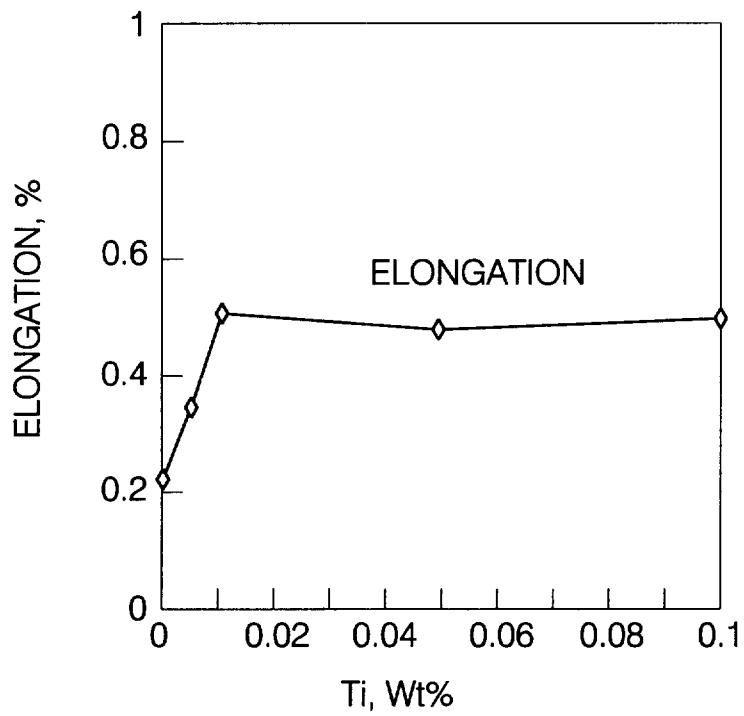
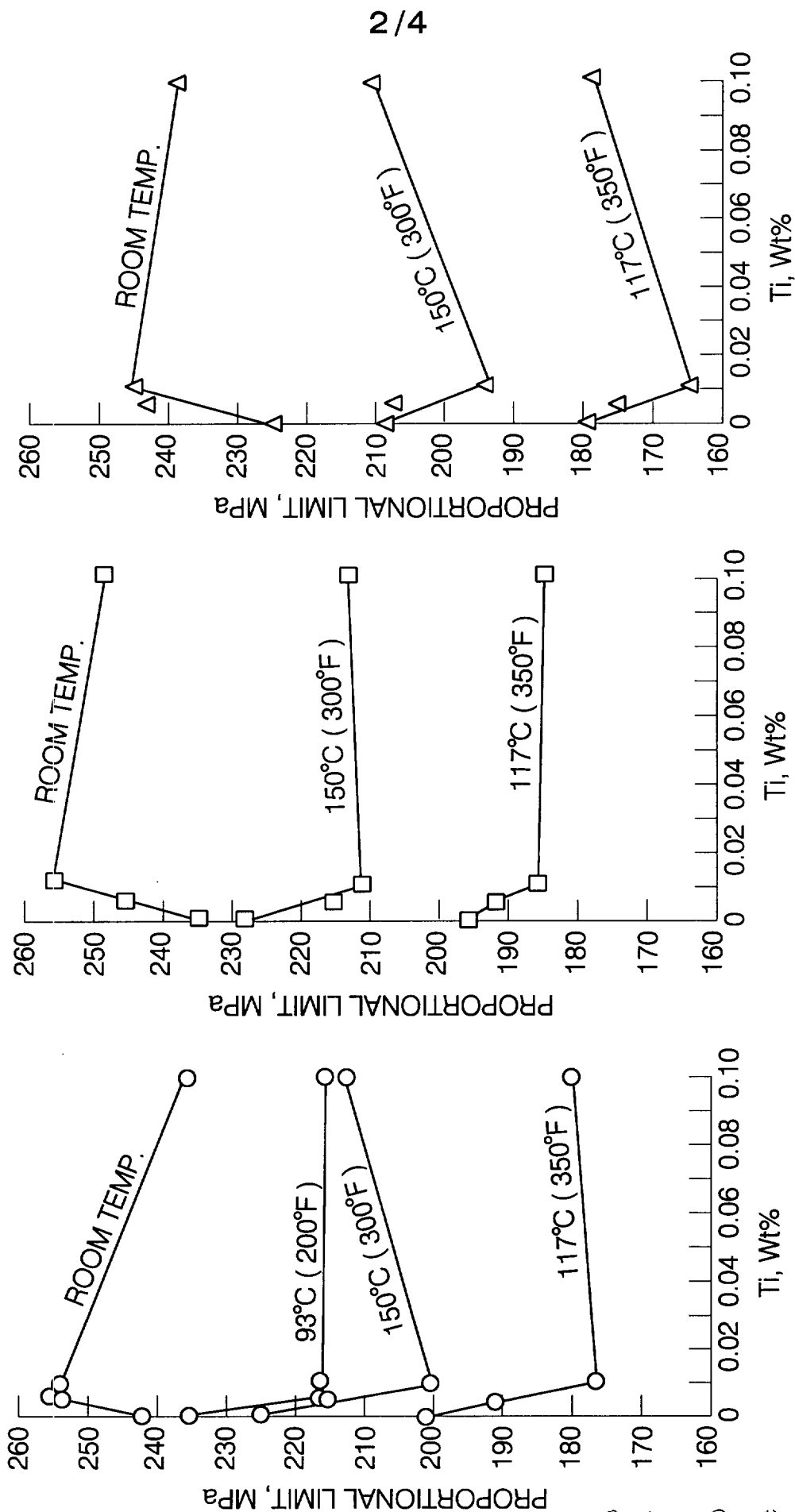


FIG. 2

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**FIG. 3C**

**FIG. 3B**

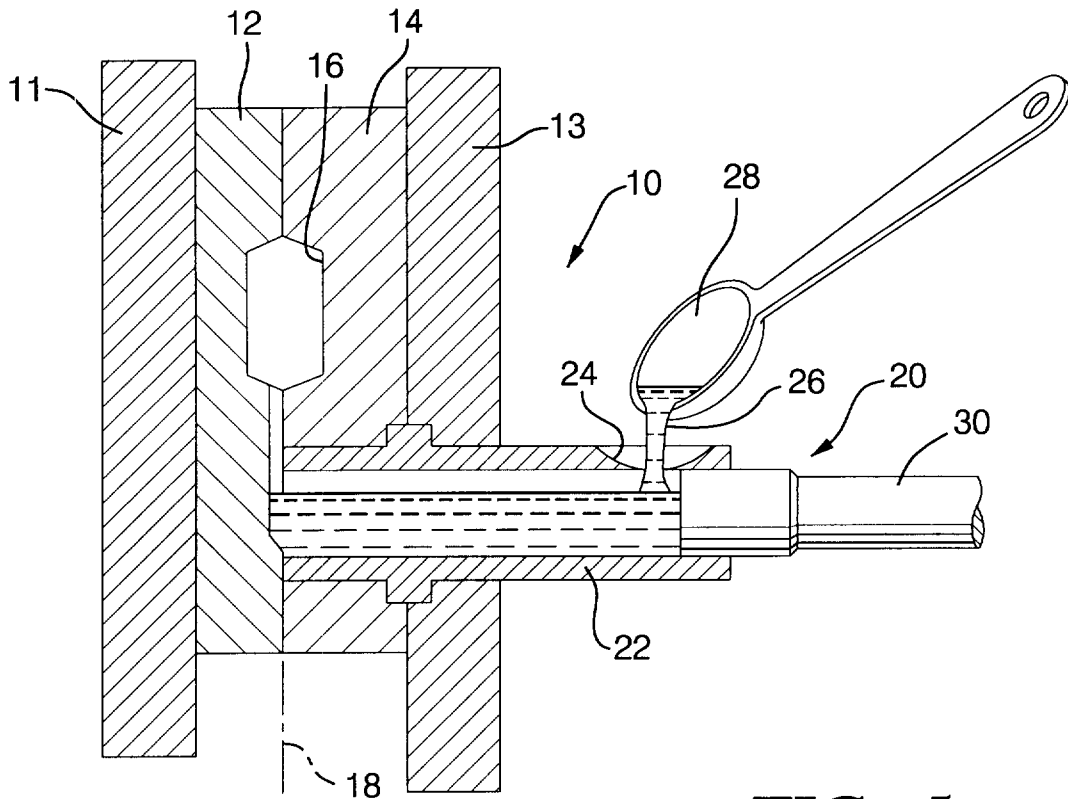
**FIG. 3A**



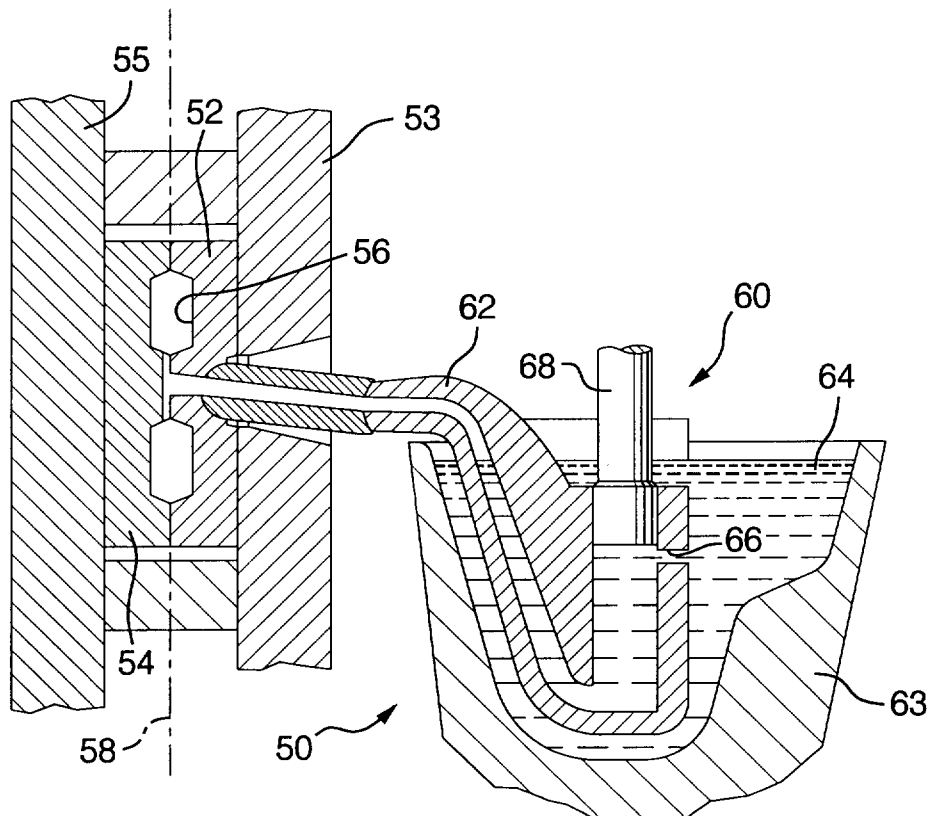
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**FIG. 5**



**FIG. 6**