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(54) **ZINC ALLOY AND MANUFACTURING METHOD THEREOF**

ZINKLEGIERUNG UND HERSTELLUNGSVERFAHREN DAFÜR

ALLIAGE DE ZINC ET SON PROCÉDÉ DE FABRICATION

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Description**TECHNICAL FIELD**

- 5 **[0001]** The invention relates to the technical field of alloys and specifically relates to a zinc alloy with excellent crack resistance and a manufacturing method thereof.

BACKGROUND

- 10 **[0002]** Zinc alloy for die casting is an alloy formed by adding other elements based on zinc. Commonly added alloying elements are aluminum, copper, magnesium, cadmium, lead, titanium, and the like. Zinc alloy has a low melting point and good fluidity and is convenient for welding, brazing and plastic processing. Zinc alloy is corrosion resistant in the atmosphere, and the residual material is easy to recycle and remelt. However, Zinc alloy has a low creep strength and is susceptible to natural aging, which may cause dimensional changes.
- 15 **[0003]** Commonly used zinc alloys for die-casting are ZAMAK3 alloy and ZAMAK5 alloy. The composition of these two alloys is relatively simple. Initially, they mainly contain zinc and aluminum, and sometimes copper is added. Such alloys have poor corrosion resistance. In order to improve the corrosion resistance, researchers introduced magnesium. As a result, it has been found that the intergranular corrosion performance was significantly improved after the addition of magnesium, and the alloy strength was improved. Therefore, the currently marketed ZAMAK3 alloy and ZAMAK5
- 20 alloy are both added with magnesium element and the amount of magnesium is controlled at 0.03-0.06%.
- [0004]** Among the alloys for die-casting, ZAMAK3 alloy has been widely used in the bathroom hardware industry due to its excellent comprehensive performance and low cost. However, for some three-way and four-way hardware products with small R angles, when using ZAMAK3 alloy, thermal cracks are likely to occur at the R angle, and the crack rate when forming is 100%. The product design is limited by customer requirements, and the R angle cannot be modified at
- 25 will, and thus the crack cannot be resolved. Compared with ZAMAK3 alloy, ZAMAK5 alloy has higher hardness and strength, and lower flexibility. However, this alloy also has similar defects as ZAMAK3 alloy that is prone to hot cracks. DE 2142685 A1 discloses so-called superplastic zinc alloys that are processable with little effort and without crack formation. In the superplastic state, the resistance of such zinc alloys to deformation is low, so that when tensile strain of several 100% is used even 1000 to 2000% of the original length can be achieved. Zinc alloys are rendered superplastic
- 30 by thermal-mechanical treatment above half their absolute melting temperature. It is furthermore disclosed in DE 2142685 A1 that a significant increase in the creep strength can be achieved by subsequent heat treatment of the product at a temperature above 275° C and subsequent slow cooling. However, the high superplasticity of the alloy is lost as a result of such a treatment. In all examples, the zinc alloys are treated by hot and cold rolling. In contrast, the zinc alloy of the present invention is cast in the molten state.
- 35 CN 108504900 A1 discloses zinc alloys with 4.3% Al, 0.007% Mg and 0.4% Cu and, respectively, 4.35% Mg, 0.001 % Mg and 0.45% Cu.

SUMMARY

- 40 **[0005]** In order to overcome the above shortcomings of the prior art, the inventor of the present application has conducted thorough research on the existing zinc alloys and provided a method for producing a zinc alloy as specified in claims 1-4 with excellent thermal crack resistance. The zinc alloy has excellent comprehensive properties. In particular, the thermal crack resistance is significantly improved, which can meet the high surface quality requirements of castings, especially die-castings, and can also be used in recast castings. It is suitable for the production of components of
- 45 plumbing and sanitary ware, hardware accessories, electronic appliances, toys, and the like. The alloy can significantly increase the product forming yield rate, reduce the abnormal processing time of the product, and effectively increase the production capacity, thereby improving the market competitiveness of the product.
- [0006]** The purpose of the present application is achieved through the following technical solutions.
- [0007]** The present application provides a method for producing a zinc alloy with excellent crack resistance, wherein
- 50 the alloy contains Al at an amount of 3.9-4.1 wt% and Mg at an amount of 0.005-0.018 wt%, optionally Cu at an amount of 0.2-1.0 wt%, and the rest of the alloy is Zn and unavoidable impurities. The zinc alloy is obtainable by a method comprising the following steps: weighing zinc ingots, aluminum ingots, magnesium ingots and/or selectively added electrolytic copper according to the composition of the zinc alloy; adding the aluminum ingots, and/or selectively added electrolytic copper, and 1/3 of the zinc ingots at a bottom of a furnace, stirring evenly after all materials are melted,
- 55 adding the remaining zinc ingots, and using a bell to press the magnesium ingot to the bottom of the furnace at about 540°C after the materials are all melted, after the magnesium ingot is melted, adding selectively a refiner, adding a purifying agent for purifying after the refiner is fully reacted, then removing residue and gas, allowing a product to stand after a composition test is qualified, and casting boat-shaped ingots after slagging and taking out of the furnace, wherein

the refiner is a salt refiner containing a titanium salt or a boron salt or a composite of both, and is not an intermediate alloy containing RE or Zr or B.

[0008] Preferably, the amount of Mg in the alloy is 0.005-0.015 wt%. Preferably, the amount of Cu in the zinc alloy is 0.5-1.0 wt%. Preferably the alloy does not contain Zr, Sb, Cr, Mn, Ti, Bi, Se, Ni and the like, except that these elements are present as impurities in the zinc alloy each with an amount of less than 0.001 wt%.

[0009] Using the refiner of the present application can achieve the refining effect of the master alloy while ensuring good polishing performance. The problem of polishing hardpoints caused by the use of intermediate alloy containing RE or Zr or B can be avoided. Thus the mirror polishing contour requirements can be met.

[0010] In the zinc alloy of the present application, aluminum is the main alloy element, which functions to prevent the oxidation of zinc liquid, improve the surface quality of the casting, reduce the brittleness of the casting, and reduce the corrosion of zinc to the iron crucible. In addition, the addition of aluminum can also modify the grains and improve the strength and hardness of the alloy. The Al amount of the present application is 3.9-4.1 wt%. When the Al amount is less than 3.5 wt%, the fluidity of the alloy becomes poor, and the casting molding defect rate increases.

[0011] Adding magnesium to the zinc alloy of the present application can significantly reduce the intergranular corrosion tendency of the alloy and improve the corrosion resistance of the alloy. This is also the meaning of the initial addition of magnesium. The addition of magnesium by those skilled in the art is generally controlled at 0.03-0.06%. This amount is not high in the entire alloy system. Therefore, those skilled in the art usually do not pay attention to the influence of this amount. In the initial development of the present application, the inventors did not actually pay attention to the influence of this element, and mainly considered the influence of other main elements on alloy properties. However, it was found that the control of other elements could not solve the defect of hot cracking. In an accidental experiment, the inventor added an insufficient amount of magnesium and found that no hot cracking defect occurred. Therefore, the inventor began to study the influence of magnesium on zinc alloys. It was found that magnesium can not only modify the crystal grains and increase the strength of the alloy but more unexpectedly, by controlling the amount of magnesium, the defects of hot cracks can be significantly overcome. In the present application, the amount of Mg is controlled at 0.005-0.018 wt%. When the amount of Mg is less than 0.005 wt%, the alloy has poor corrosion resistance and reduced dimensional stability. When the amount of Mg is higher than 0.018 wt%, the alloy has an obvious hot cracking tendency and decreased plasticity.

[0012] The selective addition of a small amount of copper to the zinc alloy of the present application can improve the fluidity of the alloy and increase the strength of the alloy, and also help to improve the hot crack resistance of the alloy. The amount of Cu amount added is controlled at 0.2-1.0 wt%. On the one hand, a higher Cu amount increases the cost of raw materials. On the other hand, as the Cu amount increases, although the strength of the alloy increases, it increases the intergranular corrosion tendency of the alloy.

[0013] When the elements Zr, Sb, Cr, Mn, Ti, Bi, and Se in the present application exist as impurities, the amount of any single element is less than 0.001 wt%. This is of great significance for ensuring the high-quality polishing performance of the alloy and reducing the tendency of forming cracks and intergranular corrosion.

[0014] Compared with the prior art, the zinc alloy of the present application has at least the following beneficial effects:

[0015] The zinc alloy produced by the method of the present application has a significant thermal crack resistance effect. Compared with the commonly used ZAMAK3 and ZAMAK5 alloys, the thermal crack defect rate can be reduced by more than 50%, and the abnormal processing time of the product can be reduced, thereby effectively increasing the production capacity and improving the market competitiveness of the product.

[0016] The zinc alloy resulting from the method of the present application has significant thermal crack resistance and polishability, and excellent electroplating performance. The alloy can meet the high surface quality requirements of castings, and is suitable for die-casting production of components of plumbing and bathroom accessories, small hardware accessories, electronic appliances, toys, and the like, and is especially suitable for cast products prone to hot cracks.

DETAILED DESCRIPTION OF EMBODIMENTS

[0017] The present application will be further described in detail below in conjunction with specific embodiments and drawings.

Example

[0018] The compositions of the alloys of the present application and the comparative alloys are shown in Table 1.

[0019] The alloy of the present application and the comparative alloy are prepared according to the following steps: weighing zinc ingots, aluminum ingots, magnesium ingots and selectively electrolytic copper according to the composition of the zinc alloy; adding the aluminum ingots, and selectively electrolytic copper, and 1/3 of the zinc ingots at the bottom of a furnace, stirring evenly after all materials are melted, adding the remaining zinc ingots, and using a bell to press the magnesium ingot to the bottom of the furnace at about 540°C after the materials are all melted, after the magnesium

ingot is melted, selectively adding a refiner; which may be titanium salt, adding a purifying agent for purifying after the refiner is fully reacted, then removing residue and gas, allowing a product to stand after a composition test is qualified and casting after slagging and taking out of the furnace.

[0020] The alloy of the present application is a boat-shaped ingot for remelting.

[0021] Performance testing of the alloy of the present application and the comparative alloy is carried out. The specific performance testing items and basis are as follows:

1. Casting performance

[0022] The flow length of the melt is measured using a spiral specimen commonly used in casting alloys, and the fluidity of the alloy is evaluated, which is used to evaluate the casting performance of alloys 1-8 of the present application and comparative alloys 1-6. All samples are cast by hand, and the casting temperature is $420^{\circ}\text{C} \pm 2^{\circ}\text{C}$. The results are shown in Table 2.

2. Resistance to hot crack of the product

[0023] The same mold, the same die-casting machine, the same die-casting parameters, the same operator are used to die cast the alloy 1-8 of the present application and the comparative alloy 1-6 to form the same product, with a die-casting temperature of $420^{\circ}\text{C} \pm 10^{\circ}\text{C}$. The defective rates regarding die-casting cracks are shown in Table 2.

3. Polishing performance

[0024] The castings are polished separately, and then observed with naked eyes. If there are no hard spots, the result is excellent and indicated by "O"; if the total number of hard spots is more than 3, and the diameter of each hard spot is less than 0.5 mm (0.01969 inch), the result is bad and indicated by "×." The results are shown in Table 2. Example alloys 1,2 and 4 fall outside the scope of protection.

Table 1 The composition of the alloys of the present application and the comparative alloys (wt%)

Example		Al	Mg	Cu	Other elements	Refiner	Zn
Alloys of the present application	1	3.50	0.005			added	the remainder
	2	3.70	0.01				the remainder
	3	3.90	0.007				the remainder
	4	4.30	0.01				the remainder
	5	4.1	0.015	0.2			the remainder
	6	3.90	0.008	0.5			the remainder
	7	4.05	0.01	0.7			the remainder
	8	3.98	0.01	1.0		added	the remainder
Comparative alloy 1	ZAMAK 3	4.05	0.03			not added	the remainder
Comparative alloy 2	ZAMAK 5	3.98	0.05	0.7		not added	the remainder
Comparative alloy 3		4.08	0.04		Zr:0.04	not added	the remainder

(continued)

Example		Al	Mg	Cu	Other elements	Refiner	Zn
Comparative alloy 4		4.12	0.05	0.8	Ti:0.03	not added	the remainder
Comparative alloy 5		3.95	0.06		Mn:0.5 Bi:0.2	not added	the remainder
Comparative alloy 6		4.20	0.03		Sb:0.03	not added	the remainder

Table 2 Performances of the alloys of the present application and comparative alloys

Example		Casting performance	Polishing performance	Resistance to hot crack /hot crack defective rate
		flow length /mm		
Alloys of the present application	1	240	○	5%
	2	255	○	8%
	3	262	○	2%
	4	280	○	5%
	5	257	○	3%
	6	268	○	2.5%
	7	259	○	3%
	8	276	○	1%
Comparative alloys	1 (ZAMAK3)	251	○	100%
	2 (ZAMAK5)	243	○	90%
	3	238	×	85%
	4	240	×	80%
	5	228	○	90%
	6	234	○	75%

[0025] According to the performance test results in Table 2, it can be seen that as a casting alloy, the alloy of the present application has fluidity equivalent to that of ZAMAK3 and ZAMAK5 zinc alloys, but its resistance to hot cracking is significantly better than that of ZAMAK3 and ZAMAK5. The polishing performance of alloys 1-8 of the present application is better than that of comparative alloys 3 and 4. Among them, alloys 3, 5, 6, 7, and 8 of the present application have the best comprehensive properties such as crack resistance and polishing performance relatively. Alloys 3 and 8 of the present application which have an added refiner have better crack resistance. The crack resistance of comparative alloys 1-6 is not as good as that of the alloy of the present application. The crack resistance of comparative alloys 3-4 is relatively good, but the polishing performance thereof is poor, and thus they are not suitable for application to exterior parts of a bathroom with high polishing requirements.

[0026] In summary, the alloy resulting from the method of the present application has good casting properties, excellent crack resistance, excellent polishing, and electroplating properties, and is suitable for die-casting and gravity casting to produce components of plumbing, sanitary ware, hardware accessories, electronic appliances, toys, and the like, especially suitable for casting products prone to forming cracks.

[0027] The above-mentioned embodiments are used to explain the present application, not to limit the present application.

Claims

1. A method for producing a zinc alloy with excellent crack resistance, containing

Al at an amount of 3.9-4.1 wt%,
Mg at an amount of 0.005-0.018 wt%,
optionally Cu at an amount of 0.2-1.0 wt%,
the remainder of the alloy being Zn and unavoidable impurities,
comprising the following steps: weighing zinc ingots, aluminum ingots, magnesium ingots and/or selectively
added electrolytic copper according to the composition of the zinc alloy; adding the aluminum ingots, and/or
selectively added electrolytic copper, and 1/3 of the zinc ingots at a bottom of a furnace, stirring evenly after all
materials are melted, adding the remaining zinc ingots, and using a bell to press the magnesium ingot to the
bottom of the furnace at about 540°C after the materials are all melted, after the magnesium ingot is melted,
adding selectively a refiner, adding a purifying agent for purifying after the refiner is fully reacted, then removing
residue and gas, allowing a product to stand after a composition test is qualified, and casting boat-shaped ingots
after slagging and taking out of the furnace, wherein the refiner is a salt refiner containing a titanium salt or a
boron salt or a composite of both, and is not an intermediate alloy containing RE or Zr or B.

2. The method according to claim 1, wherein the amount of Mg in the zinc alloy is 0.005-0.015 wt%.

3. The method according to claim 1 or 2, wherein the amount of Cu in the zinc alloy is 0.5-1.0 wt%.

4. The method according to claim 1, wherein the alloy does not contain Zr, Sb, Cr, Mn, Ti, Bi, Se, Ni and the like, except
that these elements are present as impurities in the zinc alloy each with an amount of less than 0.001 wt%.

Patentansprüche

1. Verfahren zur Herstellung einer Zinklegierung mit ausgezeichneter Rissbeständigkeit, enthaltend

Al in einer Menge von 3,9-4,1 Gew.-%,
Mg in einer Menge von 0,005-0,018 Gew.-%,
gegebenenfalls Cu in einer Menge von 0,2-1,0 Gew.-%,
wobei der Rest der Legierung aus Zn und unvermeidbaren Verunreinigungen besteht, umfassend die folgenden
Schritte:

Wiegen von Zinkblöcken, Aluminiumblöcken, Magnesiumblöcken und/oder selektiv zugesetztem elektro-
lytischem Kupfer entsprechend der Zusammensetzung der Zinklegierung;
Hinzufügen der Aluminiumblöcke und/oder des selektiv hinzugefügten elektrolytischen Kupfers und eines
Drittels der Zinkblöcke am Boden eines Ofens;
gleichmäßiges Rühren, nachdem alle Materialien geschmolzen sind;
Hinzufügen der restlichen Zinkblöcke; und
Verwenden einer Glocke, um die Magnesiumblöcke an den Boden des Ofens bei etwa 540 °C zu drücken,
nachdem die Materialien alle geschmolzen sind;
Nach dem Schmelzen der Magnesiumblöcke, selektives Hinzufügen eines Raffiniermittels;
Hinzufügen eines Reinigungsmittels zum Reinigen, nachdem das Raffiniermittel vollständig reagiert hat,
dann Entfernen von Rückstand und Gas;
Stehenlassen eines Produkts, nachdem ein Zusammensetzungstest qualifiziert ist, und Gießen von schiff-
chenförmigen Blöcken nach dem Verschlacken und Herausnehmen aus dem Ofen, wobei das Raffiniermittel
ein Salzafriniermittel ist, das ein Titansalz oder ein Borsalz oder ein Gemisch aus beiden enthält, und keine
Zwischenlegierung ist, die RE oder Zr oder B enthält.

2. Verfahren nach Anspruch 1, wobei die Menge an Mg in der Zinklegierung 0,005-0,015 Gew.-% beträgt.

3. Verfahren nach Anspruch 1 oder 2, wobei die Menge an Cu in der Zinklegierung 0,5-1,0 Gew.-% beträgt.

4. Verfahren nach Anspruch 1, wobei die Legierung kein Zr, Sb, Cr, Mn, Ti, Bi, Se, Ni und dergleichen enthält, mit
einer Ausnahme, dass solche Elemente als Verunreinigungen in der Zinklegierung mit einer Menge von jeweils

weniger als 0,001 Gew.-% vorhanden sind.

Revendications

1. Un procédé de préparation d'un alliage de zinc présentant une excellente résistance à la fissuration, contenant:

Al dans une proportion de 3,9 à 4,1 % en poids,
Mg dans une proportion de 0,005 à 0,018 % en poids,
éventuellement Cu dans une proportion de 0,2 à 1,0 % en poids,
le reste de l'alliage étant constitué de Zn et d'impuretés inévitables,

comprenant les étapes suivantes : peser les lingots de zinc, les lingots d'aluminium, les lingots de magnésium et/ou le cuivre électrolytique ajouté de manière sélective selon la composition de l'alliage de zinc; ajouter les lingots d'aluminium, et/ou le cuivre électrolytique ajouté sélectivement, et 1/3 des lingots de zinc au fond d'un four, agiter régulièrement une fois que tous les matériaux sont fondus, ajouter les lingots de zinc restants, et utiliser une cloche pour presser le lingot de magnésium au fond du four à environ 540°C une fois que tous les matériaux ont été fondus, après la fusion du lingot de magnésium, ajouter sélectivement un raffineur, ajouter un agent purificateur pour la purification après la réaction complète du raffineur, puis éliminer les résidus et des gaz, laisser reposer un produit après un épreuve des compositions est qualifié, et couler des lingots en forme de bateau après la scorification et le retrait du four, dans lequel l'affineur est un affineur de sel contenant un sel de titane ou un sel de bore ou un composite des deux, et n'est pas un alliage intermédiaire contenant du RE ou du Zr ou du B.

2. Le procédé selon la revendication 1, dans lequel la quantité de Mg dans l'alliage de zinc est de 0,005 à 0,015% en poids.
3. Le procédé selon la revendication 1 ou 2, dans lequel la quantité de Cu dans l'alliage de zinc est de 0,5 à 1,0% en poids.
4. Le procédé selon la revendication 1, dans laquelle l'alliage ne contient pas de Zr, Sb, Cr, Mn, Ti, Bi, Se, Ni et autres, sauf que ces éléments sont présents en tant qu'impuretés dans l'alliage de de zinc, dont la quantité de chaque élément est inférieure à 0,001% en poids.

REFERENCES CITED IN THE DESCRIPTION

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