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Összetett anyag és eljárás ennek hőkezelésére

Az európai szabadalom ellen, megadásának az Európai Szabadalmi Közlönyben való meghirdetésétől számított kilenc hónapon belül, felszólalást lehet benyújtani az Európai Szabadalmi Hivatalnál. (Európai Szabadalmi Egyezmény 99. cikk(1))

A fordítást a szabadalmas az 1995. évi XXXIII. törvény 84/H. §-a szerint nyújtotta be. A fordítás tartalmi helyességét a Szellemi Tulajdon Nemzeti Hivatala nem vizsgálta.

COMPOUND MATERIAL AND METHOD FOR HEAT TREATING THE SAME

The invention relates to a composite material and a method for the heat treatment of a composite material, which has a base material, which can be age hardened, based on Al-Zn-Mg, and a plating, which cannot be age hardened and is provided on the base material, based on Al-Zn, in which the composite material is at least regionally solution annealed and cooled down, more particularly in an accelerated manner, and aged.

Corrosion-resistant composite materials are known from the prior art (for example: 7008 Alclad 7075 Sheet and Plate), which have a base material, which can be age hardened, based on Al-Zn-Mg-Cu and a naturally hard plating (which cannot be age hardened) provided on this base material, based on Al-Zn. An electrochemical potential difference of approximately 120 mV forms between the AA 7075 base material (AlZn5.5MgCu; electrochemical potential after T6 heat treatment approximately -740 mV/SCE) and the AA 7072 plating (AlZn1; electrochemical potential after T6 heat treatment approximately -860 mV/SCE). This potential difference is in the proposed range between 60 mV and 130 mV, to thus provide a more noble base material with sufficient cathodic protection (DE 60100724 T2). If such composite materials are heat-treated by soldering and/or welding, which also comprises natural aging or natural annealing, in addition to solution annealing and cooling, an increased risk of corrosion is displayed at the interface between base material and plating. Impairment of the chemical and mechanical properties due to delamination of the plating has been established.

The invention therefore has the object, proceeding from the prior art described at the outset, of providing a method for the heat treatment of a composite material, using which extremely high chemical and the mechanical properties of the composite materials can be ensured and/or achieved.

The invention achieves the stated object in that the mixed crystal matrix of the base material is impoverished in zinc by natural aging, more particularly by formation of $MgZn_2$ phases, and the base material thus becomes nobler such that an electrochemical potential difference of 40 mV to 130 mV thus results between the plating and the base material, which is more noble than the plating.

If the mixed crystal matrix of the base material is impoverished in zinc by natural aging, changes in the electrochemical potential difference between base material and plating can be expected, because the remaining matrix of the base material becomes nobler. Because the mixed crystal matrix is impoverished in zinc by natural annealing such that an electrochemical potential difference of 40 mV to 130 mV thus results between the plating and the base material, which is more noble than the plating, it can be ensured that the heat treatment can result in a desired electrochemical potential difference between base material and plating – for example, by variation of the parameters of the natural aging or by selection of the compositions of base material and/or plating material. The heat treatment according to the invention, which provides natural aging after the solution annealing and cooling, more particularly quenching, to thus make the base material more noble, can therefore ensure ultrahigh chemical resistance on the composite material. A delamination of the plating from the base material is therefore not a concern, which ensures uniform mechanical stability. This is also true if this composite material is subjected to a welding method and/or soldering method, more particularly brazing, and the material bond is cooled down after the joining.

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and then naturally annealed or naturally aged. In addition, the formation of $MgZn_2$ phases has proven to be particularly advantageous, because in addition to making the base material more noble, the strength thereof can additionally be increased. For this purpose, a ratio of Zn:Mg of greater than 2 can prove to be advantageous. The method according to the invention therefore results not only in comparatively high chemical resistance, but rather also mechanical resistance on the composite material, whereby the method according to the invention can be distinguished in relation to that of the prior art.

In general, it is to be noted that the specified potentials in the plating and in the base material, for example, were determined according to the standard ASTM G69 with reference to a saturated calomel electrode (SCE).

Advantageous properties can be achieved on the composite material in that an electrochemical potential difference of at least 50 mV is set. An electrochemical potential difference of 80 mV can prove to be preferable to protect the base material particularly well from corrosion.

If the mixed crystal matrix of the base material is impoverished in zinc proceeding from an electrochemical potential difference between plating and base material of less than 40 mV, an increased latitude in the ability to make the base material more noble, can be used to increase the strength of the base material and therefore also of the composite material. This is because the mixed crystal matrix of the base material can be impoverished in zinc more strongly, without it having to be a concern that an undesirably high range of the potential difference will be reached by the heat treatment. The latter can also substantially increase the method reliability, more particularly because temperature conditions of different levels are to be expected depending on the handling during soldering.

If the base material and the plating have an essentially equal electrochemical potential before the heat treatment of the composite material, the reproducibility of the method can be improved still further. For example, an $AlZn_{2.7}Mg_1$ base material having an $AlZn_{2.7}$ plating has been shown to be extremely suitable for brazing. Outstanding corrosion resistance and ultrahigh strength can therefore be ensured.

If the composite material is at least regionally solution annealed in the course of soldering and/or welding, a part of the heat treatment can be carried out via the integrally joined bonding. Simplified method conditions can thus result with respect to the solution annealing and the accelerated cooling or quenching.

A simple soldering method can result if the composite material has a solder layer, more particularly a hard solder layer, which is applied, more particularly plated, onto the plating. In addition, the plating can form a diffusion barrier between solder layer and base material, to shield the base material from undesired elements during soldering, which can come from the molten solder alloy, for example. This can be advantageous more particularly with a solder layer based on Al-Si, to avoid $MgSi$ phases having comparatively high electronegativity in the base material, and so as not to endanger the corrosion resistance of the composite material.

If the base material comprises at most 0.3 wt.% copper (Cu), the risk of low-melting-point phases, which can melt during a heat treatment, more particularly during soldering, can be kept low in the base material. The reproducibility of the method can be improved more particularly if it also comprises integrally joined bonding. A permitted low copper content, more particularly of 0.1 to 0.2 wt.%, can improve the corrosion resistance of the composite material, however.

The invention additionally has the object of providing a composite material, more particularly plated metal based on aluminum, for a method for the heat treatment thereof using a base material, which can be annealed, based on Al-Zn-Mg, and a plating, which cannot be annealed and is provided on the base material, based on Al-Zn, which can have advantageous chemical and mechanical properties, more particularly with respect to high corrosion resistance and high strength, which result under the conditions of soldering and/or welding on the composite material.

The invention achieves the stated object with respect to the composite material in that the base material comprises

1 to 2 wt.% magnesium (Mg)

2 to 4.5 wt.% zinc (Zn),

at most 0.3 wt.% copper (Cu),

optionally

up to 0.4 wt.% iron (Fe),

up to 0.35 wt.% silicon (Si),

up to 0.5 wt.% manganese (Mn), and/or

up to 0.35 wt.% chromium (Cr)

and comprises aluminum and production-related impurities as the remainder,

and the plating comprises

2 to 5 wt.% zinc (Zn),

at most 0.3 wt.% magnesium (Mg),

optionally

up to 0.1 wt.% iron (Fe),

up to 0.1 wt.% silicon (Si), and/or

up to 0.2 wt.% chromium (Cr), zirconium (Zr), scandium (Sc), hafnium (Hf), vanadium (V), and/or silver

(Ag)

and aluminum and production-related impurities as the remainder.

In general, it is to be noted that other elements of < 0.05 wt.% each and < 0.15 wt.% in total can be understood as production-related impurities.

If the plating comprises at most 0.3 wt.% magnesium (Mg), primarily due to the comparatively low Mg content in the plating, an annealing-related ZnMg₂ phase can be avoided, so that the potential of this plating, which cannot be annealed, remains essentially equal even through natural annealing.

A composite material which has a particularly high level of corrosion resistance and strength can be provided in that the base material comprises 1 to 2 wt.% magnesium (Mg) and 2 to 4.5 wt.% zinc (Zn). The contents of magnesium (Mg) and zinc (Zn) in the base material are therefore adjustable in relation to one another such that the base material, which becomes nobler as a result of impoverishment in zinc due to natural aging of its mixed crystal matrix, more particularly due to formation of MgZn₂ phases, results in an electrochemical potential difference

between plating and the base material, which is nobler than the plating, of 40 mV to 130 mV. The base material, which can be annealed, based on Al-Zn-Mg, can therefore be made more noble by natural annealing within narrow limits, to ensure a sufficient cathodic protection of the base material. In addition, the strength of the base material can also be increased by forming $MgZn_2$ phases, which can improve the durability of the composite material. According to the invention, a compromise can be made by way of the proposed Mg and Zn content between the ability to naturally anneal the base material, on the one hand, and the corrosion resistance of the composite material, on the other hand. In addition, a lower copper content in the base material of at most 0.3 wt.% can prevent low-melting-point phases from forming in the base material during welding and/or soldering and thus impairing the integrally joined bonding.

If the plating has at most 0.1 wt.% silicon (Si), comparatively strong base phases in the boundary layer between plating and base material can be nearly avoided if the composite material is subjected to a heat treatment. The corrosion resistance can be improved further if iron in the plating is set to a low level, which can be achieved by a content in this regard of at most 0.1 wt.% iron (Fe) in the plating.

Good soldering and/or welding capability of the composite material can be enabled if the plating comprises 2 to 4 wt.%, more particularly 2 to 3 wt.% zinc (Zn).

The composite material can be particularly suitable for natural aging if the zinc contents of the base material and the plating are identical.

The properties with respect to the corrosion resistance of the base material can be improved in that the base material comprises at least 0.1 wt.% copper (Cu).

Undesired precipitations at the interface between plating and base material can be further reduced or avoided in that the plating comprises up to 0.05 wt.% iron (Fe) and/or up to 0.05 wt.% silicon (Si).

The composite material can be particularly suitable for soldering if it comprises a solder layer based on Al-Si, which is provided on the plating, more particularly plated on. In addition, the plating can be used as a diffusion diaphragm between solder layer and base material.

The invention will be explained in greater detail by way of example hereafter on the basis of exemplary embodiments:

Various composite materials were produced to substantiate the achieved effects. The compositions of the studied alloys are listed in Table 1.

Composite material	base material	plating
1	AlZn4.5Mg (AA 7020)	Al99.5 (AA 1050)
2	AlZn2.7Mg1	AlZn2.7

Table 1: overview of the composite materials

The composite material 1 is a plated sheet metal known from the prior art. The composite material 2 represents an exemplary embodiment according to the invention. Both composite materials were soldered and

naturally aged or naturally annealed for eight hours. Subsequently, the mechanical properties thereof were ascertained, and the corrosion resistance thereof was studied. For this purpose, the yield strength $R_{p0.2}$ was ascertained in the tensile test and a SWAAT test was carried out according to ASTM G85, appendix A3. The obtained measured values are summarized in Table 2.

Composite material	$R_{p0.2}$ [MPa]	SWAAT test
1	140	not fulfilled
2	100	passed

Table 2: results of the studied composite materials

It is apparent according to Table 2 that the composite material 1 could not positively complete the SWAAT test. The base material of the composite material 1 was already attacked. In contrast, it was able to be established in the composite material 2 that the SWAAT test did result in a uniform attack of the plating, but the base material is nonetheless cathodically protected by the attacked plating.

In general and/or for the sake of completeness, it is to be noted that

- An aluminum alloy based on Al-Zn or based on Al-Zn-Mg can be a wrought alloy of the 7xxx alloy series, i.e., having zinc as the main alloy elements, or also a cast alloy of the 7xxx series (EN AC-7xxx), i.e., having zinc as the main alloy element.
- An Al-Zn-Mg (Cu) wrought or cast alloy can also be counted as an aluminum alloy based on Al-Zn-Mg.
- An aluminum alloy based on Al-Zn or Al-Zn-Mg can certainly also be used for a wrought and/or cast alloy, wherein composite materials which are reinforced by particles or fiber material are also not excluded in this case.

1. Összetett anyag, különösen Al alapú plattírozott (fémrel bevont) fémlemez, hőkezelési eljáráshoz egy Al-Zn-Mg alapú öregíthető alapanyag és egy az alapanyagra felvitt Al-Zn alapú nem öregíthető bevonófém alkalmazásával, azzal jellemezve, hogy az alapanyag tartalmaz

1-2 tömeg% magnéziumot (Mg)

2-4,5 tömeg% cinket (Zn),

legfeljebb 0,3 tömeg% rézet (Cu),

adott esetben

legfeljebb 0,4 tömeg% vasat (Fe),

legfeljebb 0,35 tömeg% szilíciumot (Si),

legfeljebb 0,5 tömeg% mangánt (Mn) és/vagy

legfeljebb 0,35 tömeg% krómot (Cr),

és a fennmaradó részt alumínium és az előállításból adódó szennyezőanyagok teszik ki,

és a bevonófém tartalmaz

2-5 tömeg% cinket (Zn),

legfeljebb 0,3 tömeg% magnéziumot (Mg),

adott esetben

legfeljebb 0,1 tömeg% vasat (Fe),

legfeljebb 0,1 tömeg% szilíciumot (Si) és/vagy

legfeljebb 0,2 tömeg% krómot (Cr), cirkóniumot (Zr), szkandiumot (Sc), hafniumot (Hf), vanádiumot (V) és/vagy ezüstöt (Ag),

és a fennmaradó részt alumínium és az előállításból adódó szennyeződések teszik ki.

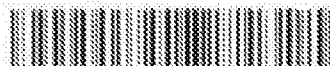
2. Az 1. igénypont szerinti összetett anyag, azzal jellemezve, hogy a bevonófém tartalmaz 2-4 tömeg%, különösen 2-3 tömeg% cinket (Zn).

3. Az 1. vagy 2. igénypont szerinti összetett anyag, azzal jellemezve, hogy az alapanyag és a bevonófém cinktartalma azonos.

4. Az 1-3. igénypontok bármelyike szerinti összetett anyag, azzal jellemezve, hogy az alapanyag legalább 0,1 tömeg% rézet (Cu) tartalmaz.

5. Az 1-4. igénypontok bármelyike szerinti összetett anyag, azzal jellemezve, hogy a bevonófém legfeljebb 0,05 tömeg% vasat (Fe) és/vagy legfeljebb 0,05 tömeg% szilíciumot (Si) tartalmaz.

6. Az 1-5. igénypontok bármelyike szerinti összetett anyag, azzal jellemezve, hogy az összetett anyag tartalmaz egy, a bevonófémre felvitt, előnyösen ráplattírozott Al-Si alapú forrasztóanyagot.



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7. Eljárás az 1-6. igénypontok bármelyike szerinti összetett anyag hőkezelésére, amelynek során az összetett anyagot legalább helyenként oldatban hevítjük, és előnyösen gyorsított módon lehűtjük és öregítjük, ahol az alapanyagok elegykristály mátrixát természetes öregítéssel, különösen MgZn_2 fázisok képzésével cinkben elszegényítjük, ezáltal az alapanyag nemesebbé válik, így módon 40 mV - 130 mV elektrokémiai potenciál különbség jön létre a bevonófém és a bevonófémnél nemesebb alapanyag között.

8. A 7. igénypont szerinti eljárás, azzal jellemezve, hogy legalább 50 mV, előnyösen 80 mV elektrokémiai potenciál különbséget állítunk be.

9. A 7. vagy 8. igénypont szerinti eljárás, azzal jellemezve, hogy az alapanyagok elegykristály mátrixát a bevonófém és az alapanyag között jelentkező 40 mV-nál kisebb elektrokémiai potenciál különbségtől kiindulva cinkben elszegényítjük.

10. A 9. igénypont szerinti eljárás, azzal jellemezve, hogy a összetett anyag hőkezelése előtt az alapanyag és a bevonófém elektrokémiai potenciálja lényegében azonos.

11. A 7-10. igénypontok bármelyike szerinti eljárás, azzal jellemezve, hogy a összetett anyagot legalább helyenként oldatban hevítjük a forrasztás és/vagy hegesztés folyamán.

12. Az 1-6. igénypontok bármelyike szerinti összetett anyag, különösen platírozott Al alapú fémelem alkalmazása forrasztáshoz vagy hegesztéshez ezt követő természetes öregítéssel, ahol az alapanyagban a magnézium (Mg) és cink (Zn) tartalmat oly módon állítjuk be egymáshoz, hogy az alapanyag nemesebbé válik az elegykristály mátrixának cinkben való elszegényedése következtében, amelyet természetes öregedés okoz, különösen MgZn_2 fázisok képződése útján, ami 40 mV - 130 mV elektrokémiai potenciál különbséget hoz létre a bevonófém és a bevonófémnél nemesebb alapanyag között.