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Korozija in trpežnost adhezivno vezanih tlačno litih aluminijevih zlitin

Corrosion and Durability of Adhesively Bonded High-Pressure Die Cast Aluminum Alloys

Povzetek

Tlačno litje aluminijevih zlitin je privlačen proizvodni proces za izdelavo aluminijastih delov, ki se uporabljajo v avtomobilski, gradbeni ter letalski in vesoljski industriji. Združevanje tlačno litih aluminijastih komponent z drugimi strukturnimi deli s pomočjo adhezivnih sredstev še vedno predstavlja izziv zaradi kontaminacije ploskve ulitkov z mazivi pri ulivanju, ki je neločljivo povezana s procesom, in neenakomerne porazdelitve legirnih elementov po ploskvi. V tem članku bomo poročali o razvoju univerzalnih procesov predhodne kemijske obdelave za zanesljivo proizvodnjo adhezivno vezanih tlačno litih aluminijevih zlitin. Učinkovitost procesov predhodne kemijske obdelave smo ocenili s primerjavo morfologij ploskve in kemijskih sestav, korozijskih parametrov pred kemijsko obdelavo in po njej ter adhezijskih lastnosti v primeru staranja in brez njega. Prikazana je ocena procesa razvitih predhodnih kemijskih obdelav, vključno z razmaščevanjem v raztopinah NaOH, deoksidacijo v raztopini z žveplovo kislino in fluoridom ter pomakanjem v raztopine s heksafluorotitansko kislino pri tlačno litih komponentah v industriji.

Ključne besede: tlačno litje, aluminijeve zlitine, karakterizacija ploskve, korozija, adhezivna vezava, trpežnost

Abstract

High-pressure die casting of Al alloys is an attractive manufacturing process for the production of aluminum components used in the automobile, construction and aerospace industry. Joining of high-pressure die cast aluminum components with other structural parts using adhesives is still challenging, due to the inherent contamination of casting surfaces by die lubricants and the inhomogeneous distribution of alloying elements on the surface. In this lecture we will report on the development of a universal chemical pre-treatment process for the reliable fabrication of adhesively bonded HPDC aluminum alloys. The effectiveness of chemical pre-treatment processes was evaluated by comparison of surface morphologies and chemical compositions, corrosion parameters before and after chemical treatment, as well as adhesion properties without and with aging. The validation of the developed chemical pre-treatment process including degreasing in NaOH solutions, de-oxidation in fluoride-containing sulfuric acid solutions and dipping in hexaflurotitanic acid solutions, on high-pressure die cast components from the industry will be demonstrated.

Keywords: high-pressure die casting, aluminum alloys, surface characterization, corrosion, adhesive bonding, durability

1 Uvod

Tlačno litje (HPDC) aluminijevih zlitin je privlačen proizvodni proces za lahke konstrukcijske dele v avtomobilski industriji zaradi visoke stopnje proizvodnje in nizkih stroškov izdelave delih, izdelanih s tehniko litja skoraj brez izmeta [1–3]. Adhezivno vezanje je ena najobetavnejših tehnik spajanja za vezavo neenakih materialov, kot so jekla, aluminijeve zlitine in z vlakni okrepljena plastika v hibridni konstrukciji vozil. Integracija aluminijevih ulitkov v hibridne konstrukcije za vozila s pomočjo adhezivnih sredstev še vedno predstavlja izziv zaradi kontaminacije ploskve ulitkov z ostanki maziv in neenakomerne porazdelitve legirnih elementov, ki so škodljivi za začetno trdnost vezanja in trajnost adhezivnih spojev pri tlačnem litju aluminijevih zlitin [4, 5]. Naše predhodno delo v zvezi z adhezijskimi lastnostmi tlačno litih aluminijevih zlitin je pokazalo, da je do adhezijske napake pogosto prišlo pri ploskovnih regijah, oddaljenih od lijaka taline, na teh predelih pa je bila zaradi obogatenih intermetalnih faz izmerjena visoka gostota korozijskih tokov [4]. Zato se lastnosti adhezivne vezave aluminijevih tlačnih ulitkov močno razlikujejo glede na različne lokacije na livni ploskvi. Na podlagi kemijske analize ploskve in ocene trdnosti vezanja smo razvili kemijski proces za predobdelavo tlačno litih aluminijevih zlitin za izdelavo adhezivno vezanih struktur s pomočjo tlačno litih aluminijevih komponent. Ta postopek zajema tri korake, tj. razmaščevanje v alkalnih raztopinah, deoksidacijo v kislinskih raztopinah in nanos oksidnih premazov v kopeli za kemično konverzijo na tlačno litih aluminijastih ploskvah za boljšo odpornost proti koroziji, optimiziran pa je bil v zvezi s kemikalijami, uporabljenimi v drugem in tretjem koraku [5–7]. Najučinkovitejši odkriti proces kemične obdelave zajema

1 Introduction

High-pressure die casting (HPDC) of Al alloys is an attractive manufacturing process for light-weight structural parts in the automobile industry because of the high production rate and low cost for the fabrication of near-net-shape components [1-3]. Adhesive bonding is one of the most promising joining techniques for bonding dissimilar materials, such as steels, aluminum alloys and fiber-reinforced plastics in hybrid construction of vehicles. Integration of Al die castings into hybrid vehicle-structures using adhesives is still challenging due to the inherent contamination of the casting surfaces by residual lubricants and the inhomogeneous distributions of alloying elements, which are detrimental to the initial bonding strength and durability of adhesive joints involving HPDC Al alloys [4, 5]. Our previous work on the adhesion properties of HPDC Al alloys showed that an adhesive failure often occurred in the surface regions away from the melt in-gate and that a high corrosion current density in these regions was also measured due to the enrichment of intermetallic phases [4]. Thus the adhesive bonding property of an HPDC Al casting varies significantly at different locations on the casting surface. Based on the surface chemical analysis and the evaluation of bonding strength, we have developed a chemical process for the pre-treatment of HPDC Al alloys to fabricate adhesively bonded structures using HPDC Al components. This process consists of three steps, i.e., degreasing in alkaline solutions, deoxidation in acidic solutions and deposition of oxide coatings in a chemical conversion bath on HPDC Al surfaces to improve corrosion resistance, and it was optimized with respect to chemicals used in the second and third steps [5-7]. The most effective chemical treatment process razmaščevanje v alkalnih raztopinah, ki mu sledi deoksidacija v žveplenokislinskih raztopinah s fluoridom ter nanos Ti-oksidnih konverzivnih premazov. V tem članku poročamo o uporabi optimiziranega procesa predobdelave pri drugih tlačno litih ulitkih z različnimi sredstvi za mazanje pri ulivanju. Učinkovitost procesa predobdelave smo potrdili z oceno trajnosti adhezivnih spojev pred staranjem in po njem.

2 Materiali in preizkusne metode

Dve aluminijevi zlitini, EN AC-AlSi9Cu3(Fe) in EN AC AlSilOMnMg, smo predhodno stalili v električni peči in nato ulili v plošče (260 × 150 × 4 mm) z uporabo livarskega stroja za tlačno litje (Buehler Evolution 530B). Med procesom tlačnega litja smo livne ploskve pri vsakem livnem ciklu popršili s sredstvi za mazanje na osnovi polisiloksana z dodatkom voska ali brez njega (ChemTrend, Nemčija).

Kemikalije, uporabljene pri predobdelavi tlačno litih aluminijevih zlitin, so navedene v Preglednici 1. Te kemične raztopine so bile izbrane izmed komercialno dostopnih industrijskih izdelkov na osnovi njihovih glavnih sestavin (Alufinish GmbH, Nemčija). Morfologijo ploskve in kemijsko sestavo pred kemijsko obdelavo in po njej smo preverili z vrstično elektronsko mikroskopijo (SEM: JEOL JSM6480) in rentgensko fotoelektronsko spektroskopijo (XPS: ESCA-Lab MK II).

found consists in degreasing in alkaline solutions, followed by deoxidation in fluoride-containing sulfuric acid solutions and deposition of Ti-oxide conversion coatings. In this paper we report on the applicability of the optimized pre-treatment process to other HPDC alloys cast with different die lubricants. The effectiveness of the pretreatment process was verified by the evaluation of the durability of adhesive joints before and after aging.

2 Materials and Experimental Methods

Two Al alloys, EN AC-AlSi9Cu3(Fe) and EN AC AlSi10MnMg were pre-melted in an electric furnace and then cast into plates (260 x 150 x 4 mm) using an HPDC machine (Buehler Evolution 530B). During HPDC process, polysiloxane-based die lubricants with or without wax-additives (ChemTrend, Germany) were sprayed onto the die surfaces in each casting cycle to maintain HPDC operation.

The chemicals used for the pre-treatment of HPDC Al alloys are listed in Table 1. These chemical solutions were selected from commercially available industrial products based on their main ingredients (Alufinish GmbH, Germany). The surface morphology and chemical compositions before and after chemical treatment were examined by using scanning electron microcopy (SEM: JEOL JSM6480) and X-ray photoelectron spectroscopy (XPS: ESCA-Lab MK II), respectively.

Preglednica 1. Glavne kemikalije, uporabljene za predobdelavo ploskve

Table 1. Main chemicals used for surface pre-treatment

Razmaščevanje / Degreasing	Deoksidacija / Deoxidation	Konverzivni premaz / Conversion coating
raztopina NaOH / NaOH solution	Raztopina F- + H_2SO_4 / F- + H_2SO_4 solution	Raztopina H_2TiF_6 / H_2TiF_6 solution

Za izdelavo vzorcev klinaste oblike skladno z nemškim standardom DIN 65448 je bilo uporabljeno enokomponentno konstrukcijsko lepilo na osnovi epoksija (Dow Automotive System). Po 30-minutnem strjevanju pri temperaturi 180 ºC so bile tlačno liti paneli iz vsake plošče izrezani v štiri vzorce klinaste oblike. Po vstavitvi vzorcev klinaste oblike in skladiščenju v laboratorijski atmosferi 1 uro smo izmerili dolžino začetne napokline. Nato smo vzorce klinaste oblike v klimatski komori za 1 teden potopili v raztopino NaCl (5 wt%) pri temperaturi 70 °C. Po staranju smo znova izmerili dolžino napokline. Po obnovi na zraku pri sobni temperaturi smo vzorce klinaste oblike za pregled prelomnih ploskev odprli s pomočjo stroja Instron 5567.

A one-part structural adhesive based on epoxy (Dow Automotive System) was used to fabricate wedge specimens according to the German standard, DIN 65448. After curing at 180 ºC for 30 min, the bonded HPDC panels were cut into four wedge specimens from each plate. After the insertion of the wedges and storage in the lab atmosphere for 1 h, the initial crack length was measured. Then, the wedge specimens were immersed in 70 °C, 5 wt% NaCl solutions in a climate chamber for 1 week. After aging the crack length was measured again. After reconditioning at room temperature in air, the wedge specimens were opened using an Instron 5567 machine for examination of fracture surfaces.

3 Rezultati in razprava

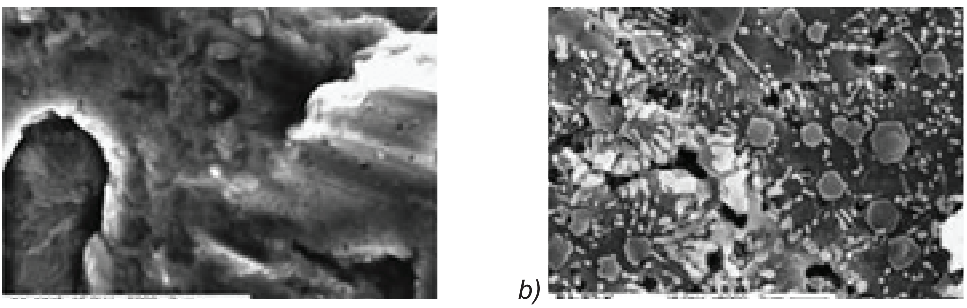
3.1 Spremembe v morfologiji ploskve in kemijski sestavi po kemijski obdelavi

Sprememba v morfologiji ploskve po kemijski obdelavi tlačnega litja AlSi10MnMg je prikazana na Sl. 1. Relativno nezanimiva

3 Results and discussion

3.1 Changes in Surface Morphology and Chemical Compositions after Chemical Treatment

The change in surface morphology after the chemical treatment of HPDC AlSi10MnMg is shown in Fig. 1. The relatively featureless



a) b)

Sl. 1. SEM mikroposnetki na ploskvi tlačno litih plošč AlSi10MnMg: (a) pri litju in (b) po kemični obdelavi

Fig. 1. SEM micrographs of the surface of HPDC AlSi10MnMg plates: (a) as-cast and (b) after chemical treatment

morfologija ploskve pri ploskvi med litjem se je spremenila v grob vzorec z izpostavitvijo intermetalnih faz, delcev Si in tvorbo jamičastih korozij na kristalnih mejah zaradi učinkov jedkanja uporabljenih kemikalij. Kemijska sestava ploskve, določena na podlagi meritev XPS, je prikazana na Sl. 2.

Po kemični obdelavi je koncentracija pri vrstah, ki vsebujejo C, pri ploskvi pri litju padla s približno 65 at% na približno 40 at% na kemično obdelanih ploskvah skupaj z zvečanjem koncentracije atomov kisika in aluminija. Nanos Ti-oksidnega konverzivnega premaza smo potrdili s pojavom signalov Ti (približno 0,5 at%) na posnetku preiskave kemično obdelane

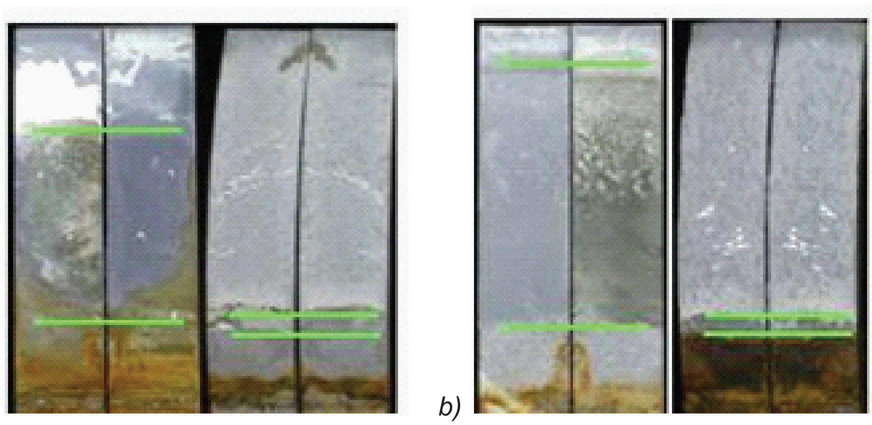
surface morphology of the as-cast surface changed into a rough pattern with exposure of intermetallic phases and Si particles and formation of pitting holes at the grain boundaries, due to etching effects of chemicals used. The surface chemical composition determined from XPS measurements are listed in Table 2.

After chemical treatment, the concentration of C-containing species decreased from about 65 at% on the as-cast surface to about 40 at% on chemically treated ones and is accompanied by an increase in atomic concentration of oxygen and aluminum. The deposition of Ti-oxide conversion coating was confirmed by the

Preglednica 2. Kemijska sestava ploskve (at. %) AlSi10MnMg pred kemijsko obdelavo in po njej

Table 2. Surface chemical compositions (at. %) of AlSi10MnMg before and after chemical treatment

	C	O	Si	Al	Mg	F	Ti
pri litju / as-cast	65,2	14,7	11,8	4,6	3,7	0,0	0,0
kem. obd. / chem.	40,3	30,2	6,9	20,7	0,7	0,7	0,5



a) pri litju / as-cast kem. obd. / chem. b) pri litju / as-cast kem. obd. / chem.

Sl. 2. Prelomne ploskve vzorcev v obliki klinov, v litem stanju in kemično obdelane (kem. obd.) stanju (a) tlačno lite zlitine AlSi10MnMg in (b) tlačno lite zlitine AlSi9Cu3(Fe). Razširitev napokline je na vsaki fotografiji označena z zelenimi črtami.

Fig. 2. Fracture surfaces of wedge specimens fabricated in the as-cast and chemically treated (chem.) states of (a) HPDC AlSi10MnMg and (b) HPDC AlSi9Cu3(Fe) alloys. The crack extension is marked by the green lines in each photograph

ploskve. Na eni strani je padec koncentracije Si po kemični obdelavi dodaten kazalnik za odstranitev preostalih maziv. Po drugi pa pri visoko ločljivostnem spektru Si2p pri ulivani ploskvi prevladujejo organske vrste Si, ki nastanejo zaradi preostalih maziv, medtem ko pri kemično obdelanih ploskvah prevladuj anorganski Si, tj. Si in SiO2. Rezultate karakterizacije ploskve smo potrdili z učinkovitostjo kemične obdelave za odstranitev preostalih maziv in nanosom Ti-oksidnih premazov, odpornih proti koroziji.

3.2 Ocena lastnosti začetne vezave in trajnost adhezivnih spojev

Dolžina začetne napokline, sprožene z vstavitvijo vzorcev v obliki klina, in razširitev napokline po staranju za dve tlačno liti aluminijevi zlitini sta prikazani v Sl. 3. Pri litem stanju smo opazili daljšo začetno napoklino in razširitev napokline kot pri kemično obdelanem vzorcu. Prav tako smo opazili, da legirni elementi pri tlačno litih zlitinah vplivajo samo na trajnost adhezivnih spojev, izdelanih pri litju. Po kemični obdelavi nismo opazili nobene očitne odvisnosti na zlitinsko sestavo. Ta rezultat nakazuje, da je proces kemične predobdelave primeren za predobdelavo različnih tlačno litih zlitin in je posledično univerzalni proces za adhezivno vezanje aluminijevih tlačno litih zlitin.

appearance of Ti signals (about 0.5 at%) in the survey scan of the chemically treated surface. On one hand, the decrease in Si concentration after chemical treatment is another indicator for removing residual lubricants. On the other hand, the high-resolution Si2p spectrum of the as-cast surface is dominated by organic Si species resulting from the residual lubricants while that of chemically treated surfaces is dominated by inorganic Si, i.e., Si and SiO2. The results of surface characterization confirmed the effectiveness of chemical treatment for the removal of residual lubricants and the deposition of corrosion-resistant Ti-oxide coatings.

3.2 Evaluation of initial bonding properties and the durability of adhesive Joints

The initial crack length induced by inserting wedges, and the crack extension after aging for two HPDC Al alloys are listed in Table 3. Longer initial crack length and crack extension were observed for the as-cast state than for the chemically treated specimen. It is also noticed that the alloying elements in HPDC alloys influence only the durability of adhesive joints fabricated in the as-cast state. After chemical treatment, no obvious dependence on alloying

Preglednica 3. Dolžina začetne napokline in razširitev napokline po staranju pri temperaturi 70 ºC v raztopini NaCl (5 wt. %)

Table 3. Initial crack length and crack extension after aging in 70 ºC, 5 wt. % NaCl solutions

Tlačno lita zlitina / HPDC alloy	Stanje ploskve / Surface state	Dolžina napokline (mm) / Crack length (mm)	
		Začetno / Initial	Po staranju / After aging
AlSi9Cu3(Fe)	pri litju / as-cast	29,9 ± 8,9	84,8 ± 28,0
	kem. obd. / chem.	19,3 ± 1,1	19,9 ± 1,6
AlSi10MnMg	pri litju / as-cast	31,7 ± 7,6	72,6 ± 9,4
	kem. obd. / chem.	21,6 ± 2,1	25,2 ± 6,3

Reprezentativne prelomne ploskve po odprtju vzorca klinaste oblike, izdelanega s kemično obdelavo in brez nje, so prikazane v Sl. 2 za obe tlačno liti zlitini. Prelomne ploskve adhezivnih spojev pri litju kažejo na možnost napak, ki prevladujejo pri vezavi, medtem ko kemično obdelani vzorci nakazujejo napake pri koheziji pri obeh tlačno litih zlitinah. Iz karakterizacije ploskve in primerjave lastnosti vezave litih in kemično obdelanih vzorcev lahko sklepamo, da lahko razvit proces kemične obdelave bistveno izboljša trajnost adhezivnih spojev pri tlačno litih aluminijevih zlitinah ter se lahko uporablja pri različnih adhezivnih vezavah tlačno litih aluminijevih zlitin.

4 Sklepi

V tem članku je prikazan proces kemične predobdelave za zanesljivo izdelavo adhezivnih spojev pri tlačno litih aluminijevih zlitinah. Proces kemične obdelave zajema razmaščevanje v raztopinah NaOH, deoksidacijo v žveplenokislinskih raztopinah s fluoridom in nanos Ti-oksidnih konverzivnih premazov. Učinkovitost procesa kemične predobdelave smo potrdili s karakterizacijo ploskve in preizkusi trajnosti adhezivnih spojev. Izkazalo se je, da je optimizirani kemični proces univerzalni proces predobdelave za tlačno lite aluminijeve zlitine z različnimi kemijskimi sestavami in litimi z različnimi sredstvi za mazanje pri ulivanju.

Zahvale

Izjemno smo hvaležni za finančno podporo Nemškega ministrstva za gospodarstvo in energetiko (BMWi) prek Kolektivne raziskave industrijskega združenja (IGF).

composition was observed. This result suggested that the chemical pretreatment process is suitable for the pre-treatment of different HPDC alloys, thus being a universal process for adhesive bonding of HPDC Al alloys.

Representative fracture surfaces after opening the wedge specimen fabricated with and without chemical treatment are shown in Fig. 2 for the two HPDC alloys. The fracture surfaces of adhesive joints in the as-cast state exhibit a failure mode dominated by adhesive failure while those of chemically treated specimens show a cohesive failure mode for both HPDC alloys. From the surface characterization and the comparison of bonding properties of the as-cast and the chemically pretreated specimens, one can conclude that the developed chemical pre-treatment process can substantially improve the durability of adhesive joints involving HPDC Al alloys and is applicable to various HPDC Al alloys for adhesive bonding.

4. Conclusions

A chemical pretreatment process for the reliable fabrication of adhesive joints involving HPDC Al alloys is demonstrated in this paper. The chemical pre-treatment process consists in degreasing in NaOH solutions, deoxidation in fluoride-containing sulfuric acid solutions and deposition of Ti-oxide coatings. The effectiveness of the chemical treatment process was verified by surface characterization and durability tests of adhesive joints. The optimized chemical process is found to be a universal pre-treatment process for HPDC Al alloys of various chemical compositions and cast with different die lubricants.

Acknowledgements

Financial support from the German Ministry of Economics and Energy (BMWi) through Industrial Collective Research (IGF) is greatly acknowledged.

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AKTUALNO / CURRENT

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12.-14.09. 2018	58. IFC Portorož 2018	Portorož, Slovenija
23.-27.09. 2018	73. WFC »Creative Foundry« in Generalna skupščina WFO	Krakow, Poljska
21.-22.11. 2018	VDI-Seminar »Gussteilgestaltung in der Praxis«	Düsseldorf, Nemčija
14.-15.03. 2019	45. Aachener Gießerei-Kolloquium	Aachen, Nemčija
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