Polskie Towarzystwo Materiałów Kompozytowych
Polish Society of Composite Materials

Kompozyty 11: 4 (2011) 288-293

KOMPOZYTY
COMPOSITES

Piotr Długosz[1], Paweł Darłak[1], Robert M. Purgert[2], Jerzy J. Sobczak[1*]

[1] Foundry Research Institute, ul. Zakopiańska 73, 30-418 Kraków, Poland
[2] Energy Industries of Ohio, Park Center Plaza, Suite 200 6100 Oak Tree Blvd, Independence, USA
** Corresponding author. E-mail: sobczak@iod.krakow.pl*

Otrzymano (Received) 10.05.2011

SYNTHESIS OF LIGHT COMPOSITES REINFORCED WITH CENOSPHERES

The paper presents a method of casting metal matrix composite materials based on light alloys reinforced with cenospheres. The cenospheres, which are a product of fly ash processing by flotation, were formed into porous ceramic shaped elements and subjected to pressure infiltration with a liquid metal on a specially designed hydraulic press. The infiltration process was recorded with an infra-red camera. The obtained composite samples have been tested with the following inspections: density and hardness, X-ray and microstructure. The thermography inspection showed the temperature distribution on the surface of the preheated ceramic preforms. The X-ray examination revealed in the castings a few cracks caused probably by a high value of squeeze pressure. Numerous spheres filled with a solidified metal in the microstructure images were observed. The degradation of the cenospheres was directly connected to the infiltration process parameters, namely: the temperature of the preform and molten metal, too high squeeze pressure or too invasive process of the preform preparation. Despite the anticipations, only a slight decrease in composite density in comparison to the density of the monolithic alloy has been found. However, an increase in the composite hardness has been observed. As a result of the described work, instructions for further tests, which involve slight changes in the process parameters namely: casting pressure, temperature of the molten metal and the ceramic preforms, in order to achieve proper structural and mechanical characteristics of the composite products have been established.

Keywords: cenospheres, ALFA composites, pressure infiltration

SYNTEZA LEKKICH MATERIAŁÓW KOMPOZYTOWYCH ZBROJONYCH CENOSFERAMI

Zaprezentowano metodę odlewania kompozytów metalowych bazujących na stopach lekkich, zbrojonych materiałami odpadowymi o niskim ciężarze właściwym - cenosferami. Cenosfery, stanowiące produkt uszlachetniania popiołów lotnych metodą flotacji, zostały uformowane w porowate kształtki ceramiczne i poddane ciśnieniowej infiltracji ciekłym stopem aluminium na specjalnie przygotowanej prasie hydraulicznej. Proces infiltracji rejestrowano kamerą termowizyjną. Otrzymane próbki kompozytowe poddano badaniom rentgenowskim oraz mikroskopowym. Wykonano pomiary gęstości oraz mikrotwardości. Analiza termowizyjna dostarczyła danych na temat rozkładu temperatury na powierzchni wygrzewanych wstępnie preform ceramicznych. Badania rentgenowskie ujawniły w odlewach nieliczne pęknięcia wywołane prawdopodobnie wysoką wartością ciśnienia prasowania. W obrazach mikrostruktury zaobserwowano liczne sfery wypełnione zakrzepłym metalem. Za przyczynę degradacji ścianek cenosfer uznano zbyt duże ciśnienie prasowania, wysoką temperaturę i tempo wstępnego nagrzewania preform, nagły kontakt z gorącym stopionym metalem lub zbyt dużą inwazyjność procesu przygotowania preform. Równocześnie, wbrew wcześniejszym założeniom stwierdzono jedynie nieznaczny spadek gęstości kompozytu względem stopu wyjściowego. W ramach badań odnotowano natomiast wzrost twardości kompozytu. Ostatecznie ustalono wytyczne do dalszych prób odlewniczych, przy czym zasugerowano zmianę niektórych parametrów, takich jak: ciśnienie prasowania, temperatura stopu i preformy ceramicznej, w celu poprawy charakterystyk strukturalnych i mechanicznych gotowych wyrobów kompozytowych.

Słowa kluczowe: cenosfery, kompozyty ALFA, infiltracja ciśnieniowa

INTRODUCTION

The design of metal matrix composite materials uses a wide range of concepts relating to the areas of ceramics, engineering materials, metals, energy, and even methods for waste disposal and utilisation. Composite materials fabricated as a product based on complex components characterised by different properties continue to arouse vivid interest in the circles of materials scientists, mainly due to the unique combination of properties like tensile and fatigue strength, excellent tribological characteristics, high thermal conductivity and thermal shock resistance. Composite materials in which the reinforcing phase is fly ash, and especially cenospheres extracted from it, can be used in the production of responsible durable elements for the automotive and railway industries, as well as for aviation.

In terms of microstructure, conventional fly ash is a mixture of two types of particles: microgranules (precitipator) and microspheres (cenospheres) [1-3]. According to the data presented in literature, the methods to obtain cenospheres from fly ash are divided into wet and dry. The wet method (flotation) uses solvents such as water and various separating solutions, in which the separated particles float on the liquid surface or sink to the bottom of the tank (sedimentation). Dry methods are based on the separation of fly ash particles in a gas stream (microseparators made by Matsuoka Co. Engineering. Hosokawa Micron Ltd and Co.), or regular screening on appropriate sieves is done [4]. Wet methods because of their low cost and ease of practical execution are used more often [1, 4-6]. Hollow, filled with a gas mixture only, the ceramic spheres with a wall thickness from 2 to 10 μm seem to be the best material for a reinforcing phase of very light, yet functional, composite materials with an extremely low density in the order of 0.4÷0.7 g/cm^3, compared to metals and alloys forming the matrix, whose densities reach values in the range of 1.6÷11.0 g/cm^3 [1, 5, 7, 8]. As a result of the synthesis of light metal alloys with cenospheres, one can obtain materials that have a low density typical for metallic foams, and strength of certain alloys and composite materials.

a)

b)

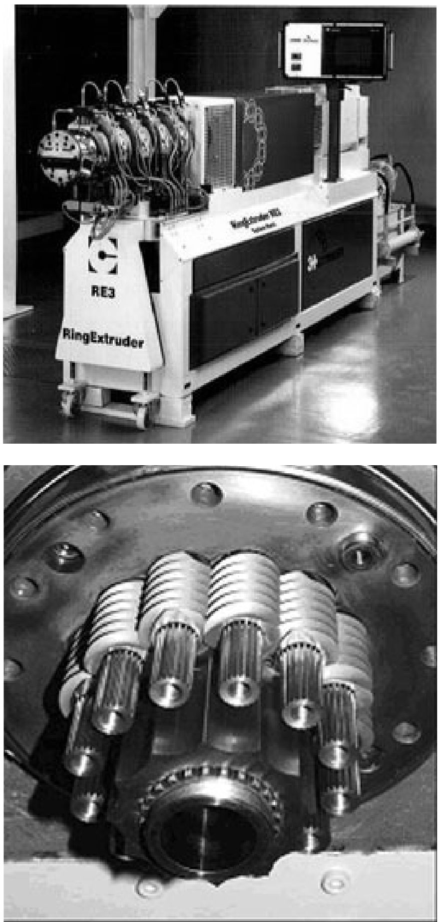


Fig. 1. a) Ring Extruder is designed for more elongational mixing vs. shear mixing for more efficient compounding, b) twelve co-rotating, fully intermeshing, self-wiping screws rotate around their own axes and do not rotate around stationary core

Rys. 1. a) RingExtruder - stanowisko do wytwarzania homogenicznych preform ceramicznych na bazie włókien i cząsteczek ceramicznych, b) głowica mieszająca składająca się z 12 mieszadeł (śrub) umożliwiających wydajne mieszanie wszystkich składników niezbędnych do wytwarzania preform ceramicznych

Depending on the manufacturing techniques of composite materials, cenospheres prepared from fly ash can be added as a component of the reinforcement in the form of loose particles, suspensions, or - so called - porous preforms. Making preforms is usually a process both difficult and costly. It consists in pressing or squeezing the material into special extruders (Fig. 1), or in soaking a specially prepared suspension of cenospheres in a solution, followed by drying and firing [9]. The preforms are usually pressure infiltrated with a liquid metallic matrix, thus becoming syntactic foams. In regards to the mechanical properties, syntactic foams significantly outperform other known cellular structures, including monolithic and composite metal foams, and can be compared to the complex mechanical characteristics of the - so called - aluminium gazars [10]. Syntactic foams based on aluminium are widely used in the automotive sector [11, 12].

Currently, one of the methods to achieve high quality parameters and strength in products made by casting (liquid-phase process) is squeeze casting. This is due to, among others, the fact that high hydrostatic pressures during the production of castings (over 200 MPa) minimise the effect of possible discontinuities in material influencing the final functional properties of the ready products. It is believed, moreover, that this is the most cost-effective and versatile process for the fabrication of composites based on light metal alloys. Other advantages of this process include high production rate, simplicity of tooling and the possibility of getting products of an exact shape and surface reproduction, which allows reduction of the necessary machining and finishing operations [9].

MATERIALS AND METHODS

For liquid metal infiltration, ceramic preforms developed in cooperation with the Century Company were used. Ceramic preforms (Fig. 2) produced in an extruder in the process of high quality homogenising mixing (Fig. 1) had a porosity of 30.2 vol. % and apparent density of 0.5 g/cm^3. The chemical composition of the manufactured preforms is shown in Figure 3.

a) b)

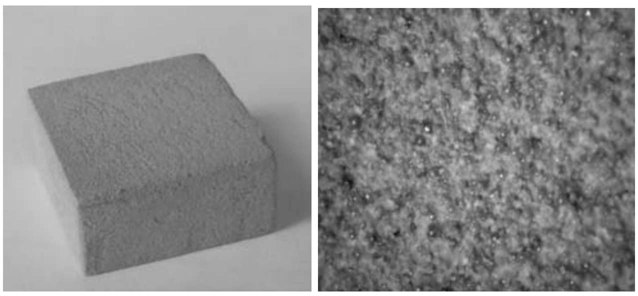


Fig. 2. a) Ceramic preform made by Century, b) preform surface

Rys. 2 a) Preforma ceramiczna firmy Century, b) powierzchnia preformy

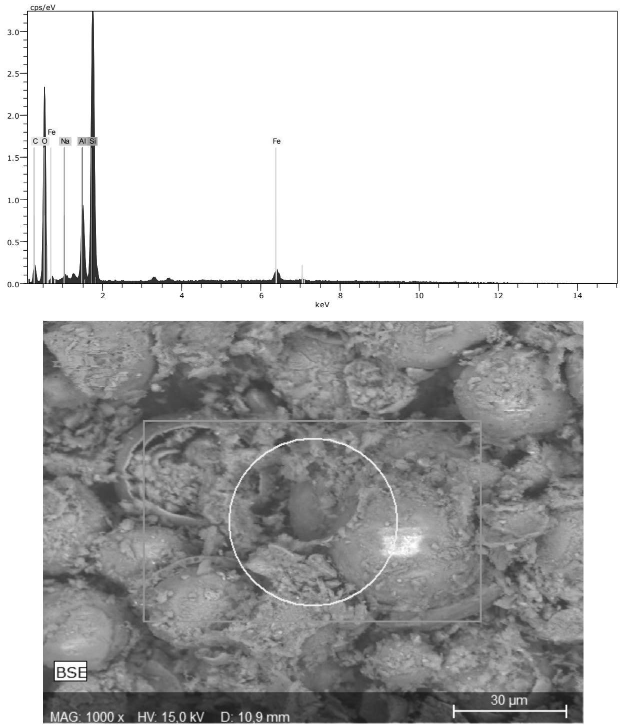


Fig. 3. Plotted diagram of EDS analysis with measuring point indicated in drawing

Rys. 3. Wykres analizy EDS wraz ze wskazaniem punktu pomiarowego na rysunku

The process of infiltration was preceded by heating of the preforms at a temperature of 800°C for 15 minutes in a specially constructed chamber oven (Fig. 4), allowing the process to be conducted in a protective atmosphere. The heating of preforms was carried out to remove moisture, which in some quantities could be left in the preform as a result of prolonged exposure to the atmospheric air, and also to counteract the rapid solidification of metal on the infiltration front, which makes the filling of open porosities with liquid metal quite impossible.

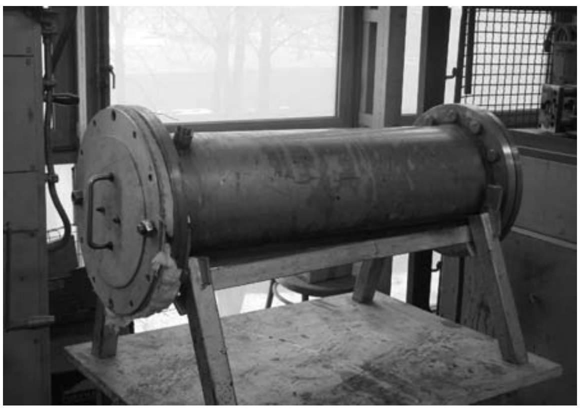


Fig. 4. View of heat treatment furnace for pre-heating preforms

Rys. 4. Widok pieca komorowego do wstępnego wygrzewania preform

Pressure infiltration of porous preforms was carried out on a stand for squeeze casting using a hydraulic press, model PHM-160C. A certain volume of a selected alloy at a temperature of 720°C was poured into the cavity of a die designed for squeeze casting (100 mm plunger diameter), pre-heated to 200°C (Fig. 5). A wrought alloy from the 7075 series (AlZn5.5MgCu) was used, as well as the same alloy modified with titanium, whose content was 0.2 wt. %. The preheated preforms were placed on the surface of the liquid alloy (upper infiltration), and then a hydrostatic pressure of a value of 120 MPa was exerted. During the tests, the alloy solidification time was measured, observing the pressure drop on squeezing. The process was also recorded by a high sensitivity 0.0035 K thermovision camera. The preset parameters are shown in Table 1.

a)

b)

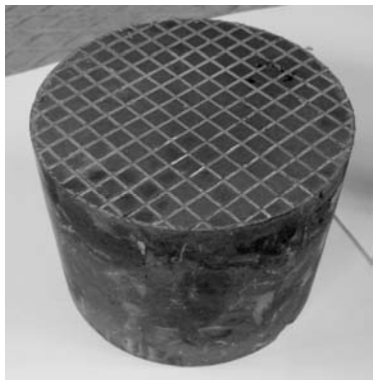


Fig. 5. a) View of die interior on stand for pressure infiltration, b) composite casting

Rys. 5. a) Widok wnętrza formy na stanowisku do infiltracji ciśnieniowej, b) odlew kompozytowy

TABLE 1. **Parameters of infiltration process**

TABELA 1. **Parametry procesu infiltracji**

Matrix material and reinforcing phase	Alloy temperature	Preform temperature in oven chamber	Squeeze pressure	Solidification time
AlZn5.5MgCu + ceno				1 min 30 s
AlZn5.5MgCu + ceno	720°C	800°C	120 MPa	2 min 30 s
AlZn5.5MgCu mod. + ceno				2 min
AlZn5.5MgCu mod. + ceno				1 min 30 s

From the castings made by infiltration (Fig. 5b), discs were cut out to be used as specimens for industrial X-ray examinations, the testing of selected mechanical properties and microstructural studies. The X-ray examinations of the castings were performed on an industrial X-ray device, type MU 2000, made by Xylon, commonly used for rapid analysis of internal casting defects. The aim of the X-ray examinations was to identify macroscopic casting defects such as cracks, shrinkage porosities and misruns. Figure 6 shows examples of images from an X-ray analysis. Only the presence of certain defects in the central part of the casting was observed. The defects might be due to the discontinuities of the ceramic preform, and those areas were filled with a monolithic alloy only (darker areas). In the case of defects due to metal contraction, the areas should have a lighter shade compared to the rest of the casting.

a) b) c)

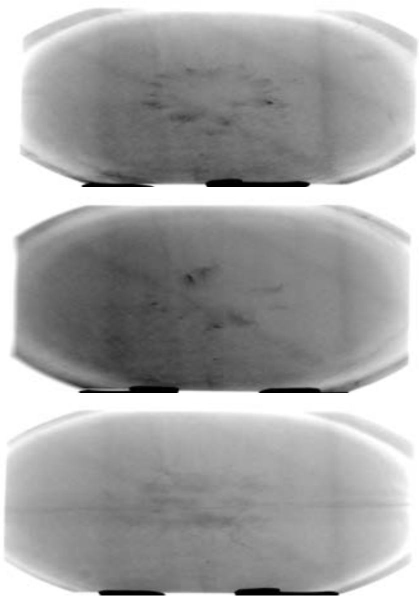


Fig. 6a-c. Result of ALFA composites X-ray inspection

Rys. 6a-c. Obrazy rentgenowskie kompozytów ALFA

Figure 6c shows a transverse fracture running through the entire width of the sample. It can prove the application of too high a squeeze pressure or too high a rate of infiltration, both of which could cause cracks in the entire volume of the preform. Another cause of this type of defect could be the difference in the coefficient of thermal expansion of the matrix material (metal) and preform (ceramics), which on solidification caused the formation of internal stresses exceeding the preform strength. However, in this case one would rather expect cracks at the matrix/composite phase boundary, and those were not found in any of the manufactured composite castings.

The thermovision analysis of the casting process carried out with a FLIR P620 camera showed the presence of temperature gradients in the ceramic specimens. A selected picture taken during the trials is presented in Figure 7. Rapid cooling of the preform during its transfer from the heating oven to the die cavity was also observed. Therefore, it seems quite reasonable to raise the preform annealing temperature, or possibly shorten the distance and time of preform transport, or use other solutions enabling continuous preheating of preforms, as well as during their transport (e.g. infra-red lamps).

a) b)

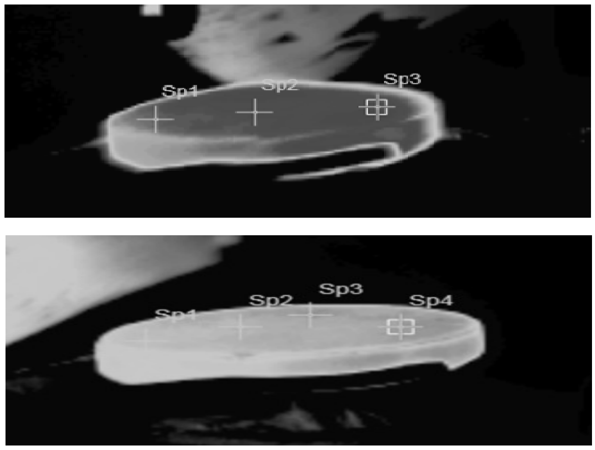


Fig. 7. Thermal analysis of infiltration process - temperature distribution in preform before infiltration; a) variant: AlZn5.5MgCu + ceno, Sp1 - 660°C, Sp2 - 667°C, Sp3 - 683°C, b) variant: AlZn5.5MgCu+ceno, Sp1 - 609°C, CSp2 - 625°C, Sp3 - 642°C, Sp4 - 646°C

Rys. 7. Analiza termiczna procesu infiltracji - rozkład temperatur w preformie na chwilę przed infiltracją; a) wariant: AlZn5.5MgCu + ceno, Sp1 - 660°C, Sp2 - 667 °C, Sp3 - 683°C, b) wariant: AlZn5.5MgCu+ceno, Sp1 - 609 °C, CSp2 - 625°C, Sp3 - 642 °C, Sp4 - 646°C

The examinations of microstructure on the composite cross-section have proved that the number of open particles filled with the matrix alloy exceeds the number of closed particles. It was found that the squeeze pressure was so high that the infiltrating metal caused degradation of the cenosphere walls. As a result, more molten alloy penetrated the composite volume, thus abating the effect of the composite reduced density in respect to the monolithic alloy (Table 2).

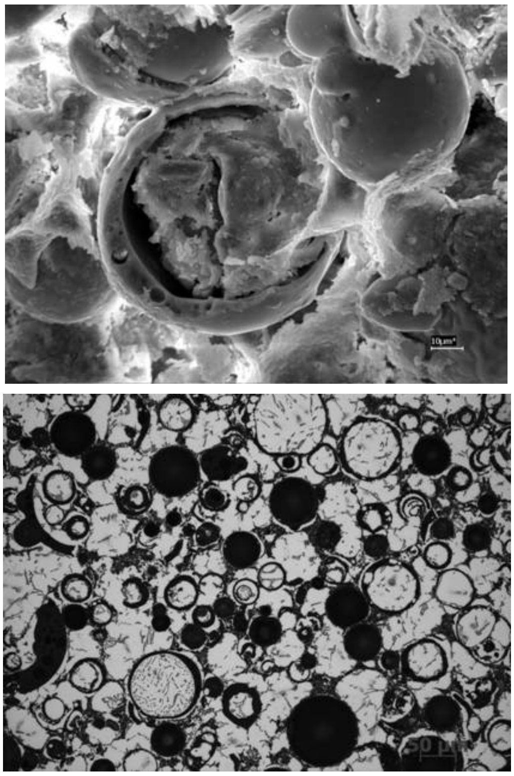
TABLE 2. **Density of preform, monolithic alloy and composite**
TABELA 2. **Wyniki pomiaru gęstości**

Material	Preform	AlZn5.5MgCu	Composite, AlZn5.5MgCu +cenospheres
Density g/cm^3	0.5	2.8	2.6
Calculated density, g/cm^3			1.2

The optical microscope and scanning electron microscope made by Hitachi TM 3000 was used in the studies (Fig. 8).

The Brinell hardness was measured at specific points on the surface of the composite plate and plate cast from the matrix material (Fig. 9).

a)



b)

Fig. 8. a) SEM analysis of cenospheres, b) microstructure of syntactic foam (AlZn5.5MgCu + cenospheres)

Rys. 8. a) Mikrostruktura preformy - mikroskop skaningowy, b) mikrostruktura piany syntaktycznej w układzie AlZn5.5MgCu + + cenosfery

a)

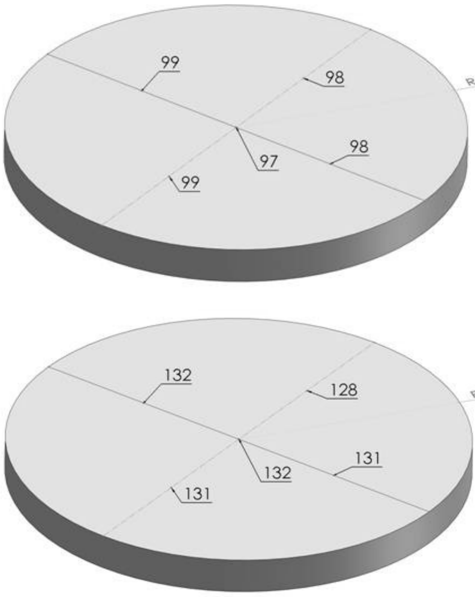


Fig. 9. Hardness comparison for AlZn5.5MgCu alloy (a) and AlZn5.5MgCu + cenospheres composite (b)

Rys. 9. Porównanie twardości stopu AlZn5.5MgCu (a) i kompozytu AlZn5.5MgCu + cenosfery (b)

Comparing the results, an increase in the composite hardness compared to the monolithic alloy was reported. The increase in hardness was mainly due to the presence of the partially degraded structure of ceramic phases in the composite material. Although the solidification mechanism in areas close to the cracked cenospheres is not completely understood, it is thought that gases which were given off during the breaking of the cenosphere walls could play an important part in the strengthening mechanism. Probably it is possible to obtain even higher values of strength properties, but only if the preform infiltration process is developed in which such drastic deterioration of the ceramic insert structure never occurs. Therefore, it seems reasonable to optimise process performance in terms of conservation of the preform structure, shape and distribution in the final composite material.

SUMMARY

The above presented technology of the fabrication of composites reinforced with cenospheres allows the production of lightweight structural material of a very beneficial homogeneous structure and mechanical properties, allowing its subsequent use in the production of ultra-thin components. The sequence of tests carried out showed that in addition to other parameters, the squeeze pressure used in the experiment can, by only careful control of its value, provide complete infiltration of ceramic preforms, while maintaining the characteristic structure of a light and robust syntactic foam.

Acknowledgements

The study was done under Project No. POIG.01.01.02-00-015/09 entitled: "Advanced materials and technologies for their manufacture", implemented under the Operational Programme Innovative Economy for the years 2007-2013.

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