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Cu BASED COMPOSITE MATERIALS REINFORCED WITH Al-Cr PREFORM PRODUCED BY REACTIVE MELT INFILTRATION

Composite materials were produced by reactive infiltration of a porous intermetallic Al₉Cr₄ preform whose structure was developed during combustion synthesis. Compacts of Al and Cr powders with a stoichiometric ratio of Al/Cr equal to 9/4 were placed and ignited in a microwave reactor. Due to the low enthalpy of the reaction, the samples were preheated. The reaction starts with partial melting of the Al particles producing a homogeneous structure with open porosity. The synthesis proceeded by intermediate phase transformations reaching a maximum temperature of ca. 1000°C. Next, the preforms were pressure infiltrated with molten Cu with interfacial diffusion of the composite elements. The intermetallic compound decomposed releasing Al which saturated the matrix and formed a Cu₉Al₄(Cr) phase. Simultaneously, the preform transformed into a mixture of globular precipitates of Cr₅₂Al₃₅Cu₁₃ embedded in the Cu₄₇Al₄₁Cr₁₂ phase. The produced composite materials exhibit significant heat and oxidation resistance. The developed protective layer was composed of Al₂O₃ oxides doped with Cr and Cu and growth with parabolic oxidation kinetics.

Keywords: reactive infiltration, preform, combustion synthesis, oxidation resistance

MATERIAŁY KOMPOZYTOWE NA OSNOWIE Cu UMACNIANE PREFORMAMI Al-Cr WYTWARZANE POPRZEZ INFILTRACJĘ REAKTYWNA

Materiały kompozytowe wytwarzano metodą infiltracji reaktywnej porowatych międzymetalicznych preform Al₉Cr₄, których strukturę wykształcono poprzez syntezę spaleniwą. Wypraskę z mieszaniny proszków Al oraz Cr o stosunku stechiometrycznym Al/Cr równym 9/4 umieszczano w reaktorze mikrofalowym, gdzie inicjowano syntezę. Z powodu niskiej entalpii reakcji próbki wstępnie podgrzewano, a reakcja rozpoczęła się od częściowego nadtopienia cząstek Al i rozprzestrzeniała na całą próbkę, tworząc jednorodną strukturę z otwartą porowatością. W trakcie syntezy powstawały fazy pośrednie, a jej maksymalna temperatura dochodziła do ok. 1000°C. Tak przygotowane preformy poddawano infiltracji ciśnieniowej ciekłą Cu, podczas której dochodziło do dyfuzji i wymiany pierwiastków pomiędzy osnową a umocnieniem. Związek międzymetaliczny uwalniał Al, które nasycało osnowę i ostatecznie tworzyło związek Cu₉Al₄(Cr). Równocześnie preforma przekształcała się w mieszaninę globularnych wydzielen Cr₅₂Al₃₅Cu₁₃ osadzonych w związku Cu₄₇Al₄₁Cr₁₂. Wytworzone kompozyty cechują się wysoką odpornością na utlenienie w podwyższonych temperaturach. W trakcie utleniania rozwija się zwarta ochronna warstewka tlenków Al₂O₃, domieszkowana Cr i Cu. Jej powolny wzrost ma charakter paraboliczny.

Słowa kluczowe: infiltracja reaktywna, preforma, synteza spaleniwą, odporność na utlenienie

INTRODUCTION

Reinforcing a Cu matrix which exhibits very good thermal and electrical conductivity improves hardness and wear resistance. Therefore, such materials are used in the production of electrical components, contacts, pantograph linings and switches [1, 2]. Copper with added Cr or Al alloying elements is characterized by high hardness, a low friction coefficient, low resistance to heat and corrosion, and can be used for strengthening coatings or composite materials [3]. Producing Cu-based composite materials by casting methods usually involves alloying the components or pressureless infiltration. To improve wetting of the reinforcement, additives like Si, Al, Cr, Ti are applied

[4]. The frequently-used chromium accumulates at the interface and as a reactive element forms a compound better wettable by the liquid Cu [5]. Recently, an intensively developing technology for composite materials is reactive infiltration processing (RIP). A porous material (preform) in contact with flowing metal undergoes transformation, changing its chemical composition and properties. Depending on the reaction kinetics, preform porosity and infiltration rate, the products may choke the flow of the metal, the complex interface may inhibit diffusion or due to the change of lattice parameters of the substrate and product, a new porosity can be formed. Therefore, the process requires precise selec-

tion of the chemical composition of the preform and infiltration parameters. Some problems can be overcome by the use of high infiltration pressures typical in the squeeze casting method. This study presents manufacturing technology based on reactive infiltration with pure Cu of porous preforms made of Al-Cr intermetallic compounds. The preforms were produced by the self-propagating high temperature (SHS) synthesis of a prepared mixture of Al/Cr powders. The obtained open porosity and chemical composition enabled reactive infiltration by the squeeze casting method.

MATERIALS AND METHODOLOGY

The production process of the composite materials includes: self-propagating high temperature synthesis SHS of porous Al-Cr intermetallic preforms and subsequent squeeze casting of them with molten Cu. The first mixture from Al (99.9% Al, 325 mesh) and Cr (99.5% Cr, 325 mesh) powders, provided by AlfaAesar, were cold isostatically pressed to produce cylindrical samples 23 mm in diameter and 5 mm in height. Next, the samples were placed in a specially designed microwave reactor to ignite synthesis and develop a porous structure. As described in detail in [6], the microwave magnetron was supplied with a constant power of 240 W. The temperature of the samples, placed in a quartz tube with argon atmosphere, was measured by a pyrometer, Raytek model Marathon MM.

The prepared preforms from the intermetallic compound Al₉Cr₄ were infiltrated with molten Cu by the squeeze casting method usually used for Al and Mg alloys. New parameters and construction of the mold were elaborated to maintain the high temperature of the composite component and prolong the infiltration time. The temperature of the preform, pouring and the die were respectively 1100, 1150 and 600°C. The infiltration pressure of was ca.100 MPa. The structures were examined with an optical and scanning microscope Hitachi TM3000 and JEOL JSM-5800LV equipped with an energy dispersive spectrometer (EDS).

EXAMINATION RESULTS

Infiltration of the porous Al-Cr preform with liquid Cu may proceed with a reaction and interdiffusion of elements from the composite components. At close contact in some places of the interface, the reaction begins between the molten copper and solid preform (melting point for Al₉Cr₄ is 1170°C). The Al atoms mainly diffuse into the matrix while the Cu penetrates the structure of preform. The reaction front moves from the interface consuming the entire structure of the Al-Cr intermetallic, see Figure 1. The process needs to maintain a relatively high temperature, which is difficult in the case of real squeeze casting infiltration. Due to the high heat transfer between the molten Cu and the die, the temperature very quickly decreases and solidifica-

tion begins almost immediately after pouring. Fortunately, during the formation of some compounds the generated heat can support the reaction. Conversion of the Cu matrix into Cu₉Al₄, whose enthalpy amounts to 503 J/kg K, releases heat for an increase in temperature ca. 20°C for an adequate volume. This can play a critical role in supporting the reaction, especially in a small volume of pores filled with liquid Cu. The low heat convection of of this liquid will increase local temperature at the interface, resulting finally in slower crystallization.

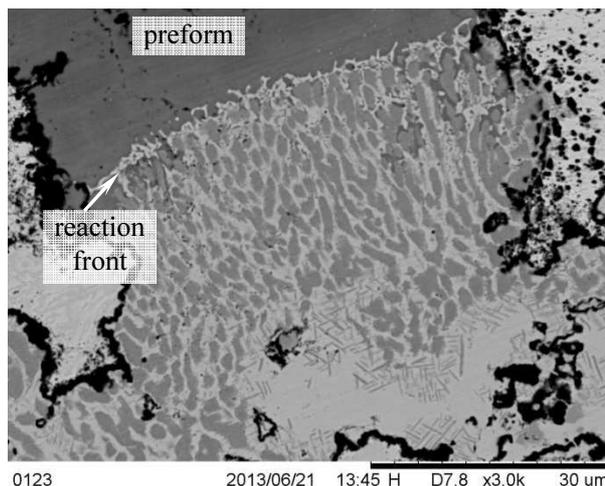


Fig. 1. Front of reaction transformed Al₉Cr₄ preform during infiltration with liquid Cu

Rys. 1. Front reakcji preformy Al₉Cr₄ ciekłą Cu podczas infiltracji

The molten matrix wetting the preform surface induces a reaction and transfer of elements. Al atoms from the preform diffuse into the liquid Cu where the intermetallic compound Cu₉Al₄(Cr) containing a small admixture of 2÷3% Cr is formed. At the beginning, as a result of the outflow of Al atoms, Al₉Cr₄ that basically forms the preform is changed into Al₈Cr₅(Cu). Simultaneously, Cu atoms crossing the interface are transferred to the preform which is gradually saturated and decomposed. Thus, in place of the preform, small globular Cr₅₂Al₃₅Cu₁₃ precipitates embedded in the Cu₅₀Al₄₃Cr₇ phase are formed beyond the moving reaction front, see Figure 2. The chemical composition of this phase corresponds to that of β phase with the space group Pm3m existing in the range between Al₄₇Cu₃₂Cr₂₁ and Al₄₅Cu₄₀Cr₁₅ [7]. With reaction progression, homogenization of the microstructure and dissolution of transitional globular grains proceed, replacing a part of the preform with a structure similar to a eutectic mixture.

Locally reinforced castings were subjected to oxidation at a high temperature with subsequent microscopic examinations of an unreinforced Cu area and composite surfaces. An intermittent isothermal test was conducted in static air at 600 and 800°C in a muffle furnace. Oxidation of the Cu castings surface involves the formation of a thick Cu₂O layer covered with thin external CuO

oxides, see Figure 3. At high temperatures ($> 500^{\circ}\text{C}$) with lattice diffusion of oxygen atoms through CuO and the absence of available vacancies for rapid transport, growth of the oxide scale is limited [8, 9].

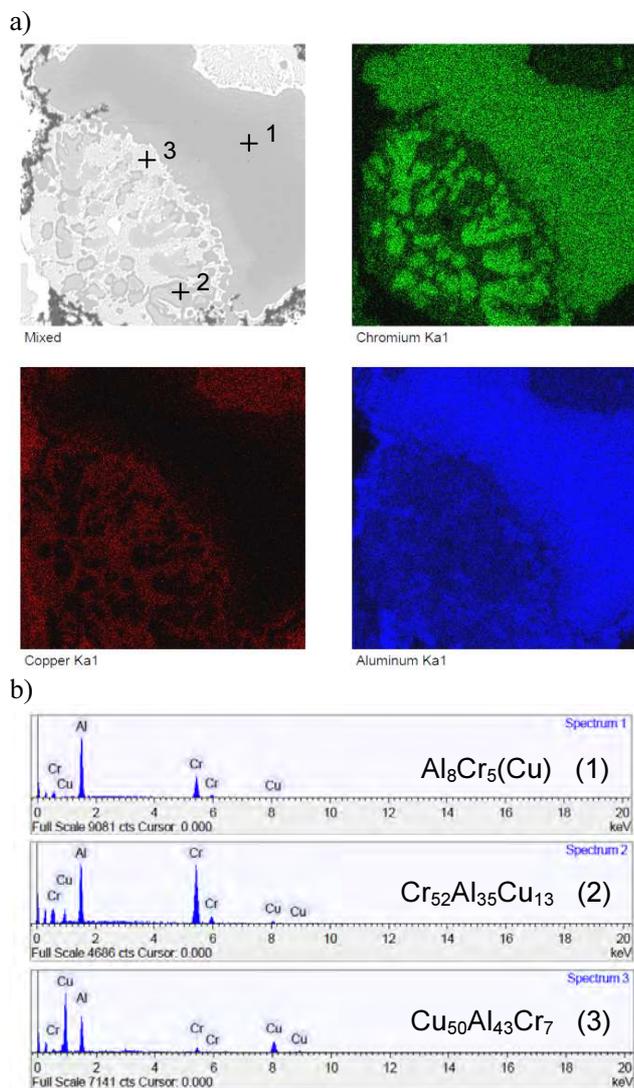


Fig. 2. Map of transformed preform elements after reactive infiltration with Cu (a), EDS analysis at marked points (b)

Rys. 2. Mapa rozkładu pierwiastków preformy podczas infiltracji reaktywnej Cu (a), analiza EDS w oznaczonych punktach (b)

Some composite samples were produced at a lower temperature, without reaction and conversion of the structure. In this case, oxidization developed mainly on the areas of a pure Cu matrix. However, growth of the Cu_2O oxide was restricted and limited in depth to the volume corresponding to small porosity filled with metal during infiltration (composite infiltrated without reaction in Fig. 4). When the conversion was completed, a small amount of Al in the Cu matrix renders developing a protective Al_2O_3 scale. Additionally, the transferred Cr atoms by mutual interaction of the elements form a thermodynamically stable layer at high temperatures, even with about 5% Al [10, 11]. Moreover, the presence of Cr prevents the growth of CuO on the alloy surface and the expansion of intercrystalline

corrosion [10]. The newly transformed composite matrix of $\text{Cu}_9\text{Al}_4(\text{Cr})$ is covered with a protective layer of oxides similarly as on the surface of a converted preform. The chemical composition of this very thin oxidized surface for both areas, the matrix and reinforcement, was almost the same, see Figure 4. It was observed that on the composite surface, a thin layer of Al_2O_3 or $(\text{AlCu})_2\text{O}_3$ oxides developed. This coincides with the results obtained by Raj [12] where on a Cu-17%Cr-5%Al alloy examined at $600\div 800^{\circ}\text{C}$, $(\text{AlCu})_2\text{O}_3$ and $(\text{AlCr})_2\text{O}_3$ scales grew respectively on the regions with Cu(Al) and $\alpha\text{-Cr}$ phases.

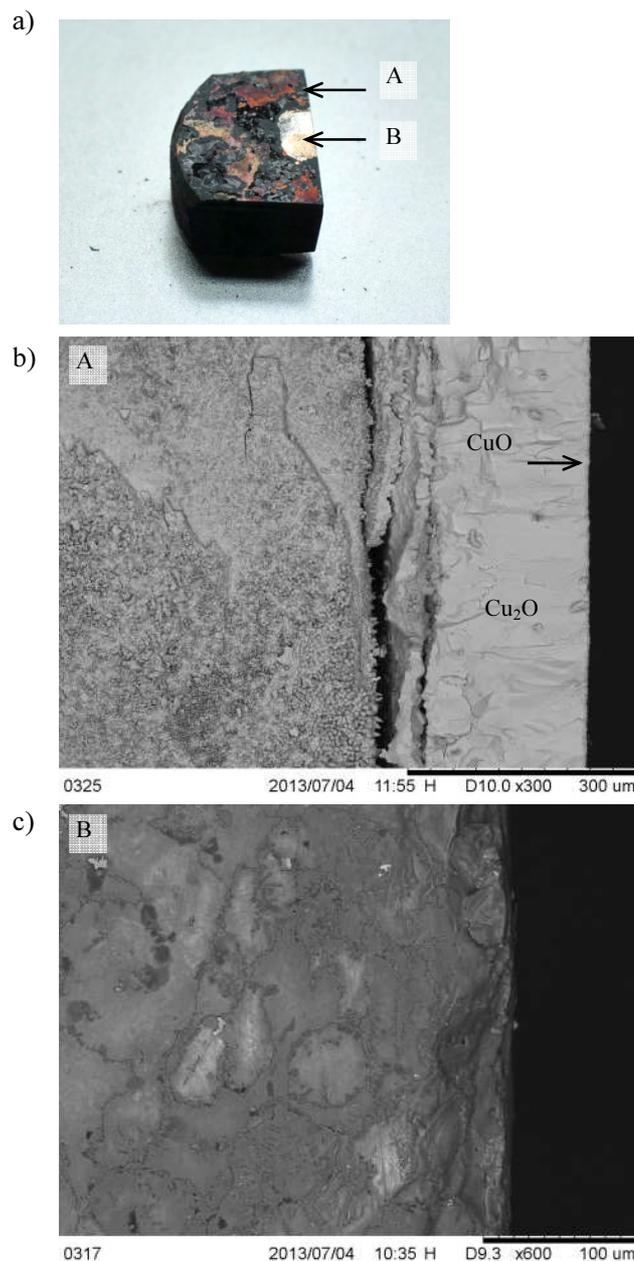


Fig. 3. Casting locally reinforced with Cr-Al preform subjected to air oxidation at 800°C (a), cross section surface of unreinforced Cu casting (b) and composite covered with thin protective layer of oxides (c)

Rys. 3. Strefowo umocniony odlew preformą Cr-Al poddany utlenieniu w temperaturze 800°C (a), przekrój powierzchni odlewu nieumocnionego Cu (b) oraz kompozytu z ochronną warstwą tlenków (c)

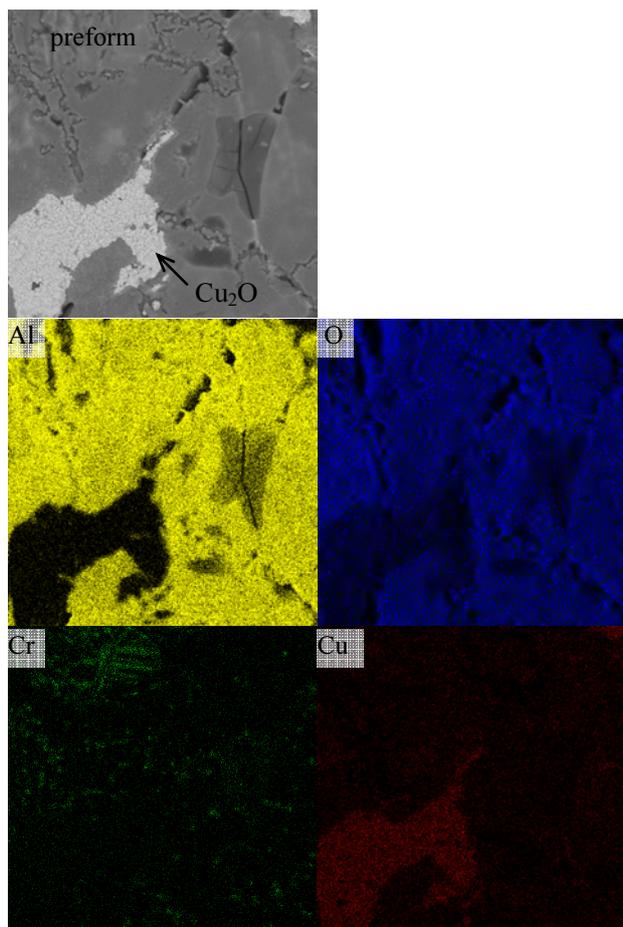


Fig. 4. Mapping of oxidized surface of composite with structure partly converted during infiltration. Al, O, Cr and Cu elements

Rys. 4. Mapa rozkładu pierwiastków Al, O, Cr i Cu na powierzchni kompozytu z częściowo przekształconą strukturą podczas infiltracji

Examination of the oxide thickness and the weight gain of the oxidized samples confirmed the high resistance of both the composites obtained without reactive infiltration (CuAlCr no reaction, see Fig. 5) and with a transformed microstructure (CuAlCr converted).

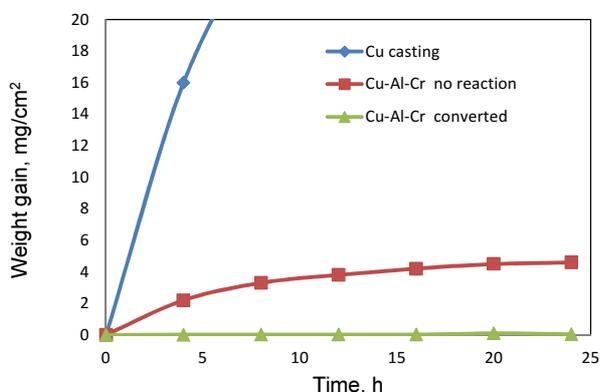


Fig. 5. Weight growth of Cu casting surface and Cu-Al-Cr composite produced by infiltration without reaction (no reaction) and composite with converted microstructure subjected to air oxidation at 800°C

Rys. 5. Przyrost masy próbki odlewu Cu oraz kompozytów Cu-Al-Cr otrzymanych bez reakcji (no reaction) oraz z całkowitą konwersją osnowy i umocnienia, poddanych utlenieniu w 800°C

The composite materials exhibit parabolic oxidation kinetics. The rate constant (k_p) calculated for the steady-state oxidation region, between 15÷25 h of the test was equal to $2.4 \cdot 10^{-2}$ and $1.9 \cdot 10^{-6} \text{ g}^2\text{m}^{-4} \text{ s}^{-1}$, respectively for the composite containing an unconverted and converted structure. By comparison, the rate constant for the oxidation of copper casting at 800°C is equal to $1.8 \text{ g}^2\text{m}^{-4} \text{ s}^{-1}$, i.e. several hundred times bigger. The surface of the composite materials with the developed new structure were covered with a compact protective layer which almost completely inhibits oxidation. Similar materials with the composition (Cu-8%Cr-2%Al) presented in [10] were characterized by a greater factor $k_p = 2 \cdot 10^{-5} \text{ g}^2\text{m}^{-4} \text{ s}^{-1}$.

CONCLUSIONS

The microstructure of the composites was developed by reactive melt infiltration of an Al-Cr intermetallic preform with liquid Cu. The porous preform was produced from compacted Al and Cr powders synthesized by self-propagation high temperature synthesis (its variant - combustion synthesis). Using the squeeze casting method, the preforms were infiltrated with molten Cu. Simultaneous reaction and transport of elements from the matrix and preform was observed. As a result of the outflow of Al and Cr from the preform, the matrix was converted into Cu₉Al₄(Cr). At the same time, Cu diffuses into the preform that gradually changed its morphology into a mixture of globular Cr₅₂Al₃₅Cu₁₃ precipitates embedded in the Cu₄₇Al₄₁Cr₁₂ phase. The obtained composites exhibit significant resistance to oxidation at high temperatures. A compact layer of Al₂O₃ doped with Cr and Cu elements was formed on the materials exposed to air oxidation at 800°C. Composite materials with a completely converted structure exhibit parabolic kinetics of oxidation at constant rate (k_p) of $1.9 \cdot 10^{-6} \text{ g}^2\text{m}^{-4} \text{ s}^{-1}$.

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