Co-continuous ceramic composites (C^4) produced by the solid-liquid interaction

Joanna Wojewoda-Budka

Metal-ceramic composites are a class of advanced materials characterized by a unique set of properties such as low density combined with the good mechanical properties such as the abrasion resistance (dispersion reinforced composites, f.e. Al-SiC, Al-Al_2O_3) and good workability (Al-graphite type of composites) [1-4]. There are number of technologies which are useful for the producing this type of composites, among them are casting, powder metallurgy, chemical and physical processes of vapor deposition and spraying. In the group of processes, which involve the liquid phase special attention is paid to *in situ* composites. They are created due to the chemical reactions between the starting components or between the gas atmosphere and a liquid metal. In this way, the problematic steps like sorting, alignment, infiltration and sintering can be avoided. Another important advantage of the resultant product is its thermodynamic stability and hence longer service life of finished products. Moreover, aluminum-alumina composites are characterized by the high hardness, thermal and electrical conductivity, thermal shock resistance and low price. This combination of unique and desirable properties is practically impossible or significantly more expensive to achieve with traditional methods of the liquid-phase composites.

The Al-Al_2O_3 composites are produced due to the presented below *redox* chemical reactions between the liquid aluminum and the ceramic oxide (MeO_y) [5]:

$$2Al+3/yMeO_y=Al_2O_3+3/yMe \qquad (1)$$

$$(x+2)Al=3/yMeO_y=Al_2O_3+Al_xMe_{3/y} \qquad (2)$$

or between the liquid aluminum and gas atmosphere:

$$4Al+3O_2=2Al_2O_3 \qquad (3)$$

$$2Al+3H_2O=Al_2O_3+3H_2 \qquad (4)$$

This can be accomplished in the casting technologies process such as the reactive liquid metal infiltration of porous ceramic preforms, production of a (Al-Me)-Al_2O_3 metal suspension by the mechanical stirring of liquid Al or its alloy with the fine-grained reactive oxide MeO [6,7], the reactive penetration of compact ceramics preforms performed by liquid metal [8-10], DIMOX process (Directed Metal Oxidation) invented by Lanxide company, in which the surface of molten aluminum alloy is oxidized due to the interaction with the oxidizing atmosphere [11-13].

The microstructure of *in situ* Al-Al_2O_3 composites is of a specific type called C^4 - **C**o-**C**ountinuous **C**eramic **C**omposites. It is constituted of two mutually interpenetrating structural components: aluminum oxide and metal (Me), Al (Me) or intermetallic phases Al_xMe_y, in which the transport of the reactants to and from the reaction front is possible. Literature reports do not provide a clear description of the structure formation mechanism.

The occurrence of the chemical reaction in which an appropriate ceramic phase is formed is certainly the absolute condition.

One of the most popular theories was proposed by Breslin [2] based on the studies of Al/SiO_2 system. He proposed *tensile cracking* mechanism of Al-Al_2O_3 composite formation assuming that initially formed thin and compact layer of alumina begins to break as a result of significant tensile stresses. These stresses in turn result from the difference in molar volume of SiO_2 substrate (1 ½ mole) and Al_2O_3 product (1 mole). Formation of a compact layer and its cracking repeat in a cycle and the spaces between the aluminum oxide are filled with liquid metal. Authors stated that the excessively high activation energy of the reduction reaction of SiO_2 (160 kJ) as for the diffusion-controlled processes together with the linear nature of the reaction kinetics confirm the mechanism proposed by them. However, a sufficient explanation for the liquid metal continuous network formation was not presented. It was only assumed that it wetted the surface of the formed oxide. Such a point of view is in contradiction with the research results carried out by a team of Prof. N. Sobczak from Foundry Research Institute in Krakow [5,14], who obtained Al-Al_2O_3 composites by the interaction between the liquid Al with the SiO_2 surface at the temperatures much lower than 1000 °C in the absence of wettability in the Al/SiO_2system.

Another theory was proposed by Loehman et al [8] on the basis of their studies on the interaction in the Al/mullite system. It is called the *reactive penetration* by the metal and involves the penetration of liquid metal along the grain boundaries of the oxide substrate. In their studies the criterion of the difference in molar volume of the substrate and product was also taken into account. Nevertheless, their close values were in this case a proof of disability to produce cracks in Al_2O_3. Loehman et al [8] assumed that the liquid aluminum wetted and penetrated the mullite's grain boundaries and then reacted with them. However, it is known that at the temperature of C^4-type microstructure formation aluminum does not wet mullite [15], and at higher temperatures it wets only the reactively formed Al-Al_2O_3.

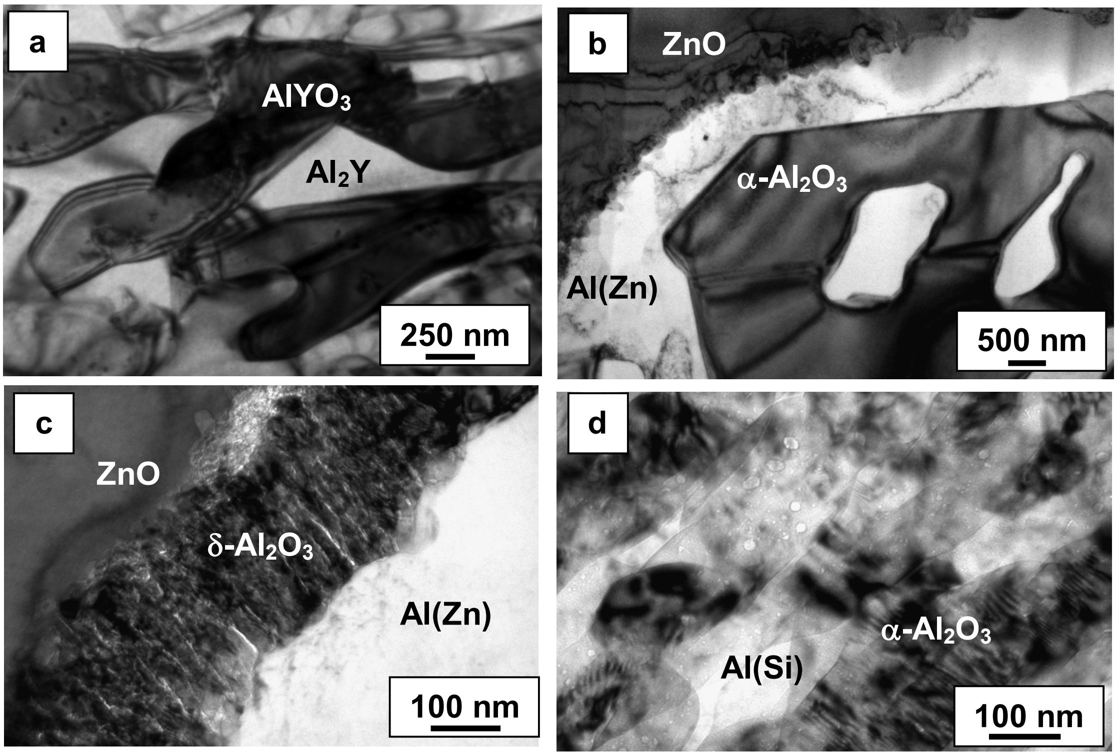
In situ Al-Al_2O_3 composites attract attention of the leading research centers both in the country and around the world. They concentrate mostly on the issues of the wettability of alumina by aluminum and its alloys, while the issue of precise characterization of the microstructure and chemical composition, especially at the nano level, remains open. Literature reports at present the data obtained mainly using the optical and scanning electron microscopy techniques. For the Al/SiO_2 system the literature reports concern only the differences in the morphology of the Al_2O_3 precipitates depending on their location: coarse - close to the aluminum drop and fine - inside the reaction products. Such a dual morphology, was also observed in the systems Al/Al_2O_3 and Al-X/Al_2O_3 (where X was the additional alloying element: Si, Cu, Ti) [16], probably due to the different formation mechanism of these precipitates. The coarse-grained Al_2O_3 are formed by the dissolution of the substrate in the liquid aluminum or Al-X alloy, and further precipitation of Al_2O_3 and its epitaxial growth. It can be assumed that in the Al/MeO systems the coarse-grained Al_2O_3 is produced in the dissolution-precipitation mechanism, whereas the fine structure of aluminum oxide is formed in the previously mentioned reaction (1) or (2). The reaction product region in the Al/SiO_2 system has a morphologically complex character [17]. Four different zones could be distinguished, however, the chemical composition analysis performed on the scanning electron microscope showed that the distribution of silicon and aluminum were similar throughout the whole reaction product zone. The introduction of the alloying elements to the aluminum resulted in the changes of both the thickness of the reaction products region and its various zones amount.

The preliminary analysis of the alumina type present within the reactively formed area in Al/SiO_2 have recently been investigated in the group of Prof. Yoshikawa [19], but their data refer only to the analysis performed on X-ray diffractometer.

On the other hand, there are also reports on Al/NiO and Al/ZnO systems [5,20]. For the Al/ZnO system there is a significant difference in the molar volumes combined with the high solubility of zinc in aluminum. This causes the presence of significant tensile stresses in the Al_2O_3 layer formed and its cracking. The obtained reaction product zone was thick and consisted of C^4 microstructure mutually interpenetrating networks: ceramic Al_2O_3 and metallic Al(Zn). Studies described in Ref. [5] showed that the aluminum oxide microstructure is coarse, but a fine-grained one can also be observed on the surface of the substrate. This is probably the reason for wetting in this system, despite the lack of wettability of ZnO by the aluminum, even at high temperatures. The reaction of aluminum with zinc oxide is unusual because of the strong zinc evaporation produced due to the reaction. As a consequence the transport of aluminum vapors from the droplet surface to the ZnO and formation of Al_2O_3 precipitates at the substrate surface is increased. Different effects have been observed for the nickel oxide substrates [5,20], which in contrast to ZnO is already wetted by aluminum at 700 °C, while ZnO does not exhibit this property even at 1000 °C. The reaction product zone composed of very small precipitates is thick and located both in the drop and the NiO substrate. In the first stage of Al-NiO interaction, a discontinuous layer of Al_2O_3 is formed due to the difference in molar volume of substrate and product. In the second stage already produced Ni reacts with Al forming Al_3Ni (at $T<855$ °C) or Al_3Ni and Al_3Ni_2 (at 855 °C$<T<$1133 °C) intermetallic phases in the channels among the alumina network [20]. The researchers have made unsuccessful attempts to infiltrate polycrystalline NiO with the liquid aluminum at 900-1200 °C [8], which was explained by the lack of wettability in the Al/NiO system.

On the other hand, Fahrenholtz [21] applying much higher process temperature of 1400 °C produced the NiAl-Al_2O_3 and Ni_3Al-Al_2O_3 composites from Al and NiO or $NiAl_2O_4$ powder mixture. Also in this case all information about the microstructure was gathered using only the conventional scanning electron microscope.

Scanning electron microscopy technique, although very useful is insufficient to collect the complete information about the product, not just the type of Al_2O_3, but also about intermetallic phases $Al_xMe_{3/y}$ formed due to reaction (2). The thickness and microstructure of the reaction product zone depend on the substrate oxide type for two reasons: the molar volume mismatch between the substrate (MeO) and product (Al_2O_3) and solubility of the produced metal in aluminum. In the frame of common projects of Ministry of Science and Higher Education and Foundation for Polish Science performed in Institute of Metallurgy and Materials Science of the Polish Academy of Sciences in cooperation with Foundry Institute from Krakow careful characterization of the reactively formed products due to the interaction between aluminum and its alloys with different oxides (SiO_2, ZnO, NiO, Y_2O_3) is performed. It will help to verify the knowledge about the both mechanisms of the C^4 microstructure formation. Transmission electron microscopy (TEM) combined with focused ion beam preparation technique allows to perform of the comprehensive research on reaction product compounds, including the Al_2O_3 type. The Figure below shows just few examples of the product morphology in different systems obtained on the TEM (TECNAI G^2) instrument being the result of the mentioned projects.



TEM images showing the differences in morphology of the reactively formed product due to the high temperature interaction between Al and Y_2O_3 (a), ZnO polycrystalline (b) and single crystal (c) and SiO_2 (d) [22-23].

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