# Ceramometal macroporous CuAlO/CuAl, CuFeAlO/CuFeAl catalysts for low temperature WGS reaction

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**Abstract:** Preparation procedure, detailed structural and textural characteristics of ceramometal catalysts are presented. These catalysts demonstrate the egg-shell microstructure, enhanced macroporosity and loading density along with volume activity in WGS reaction comparable to conventional oxide ceramic catalyst.

**Keywords:** Porous ceramometals, Properties, Activity in WGS.

## 1. Introduction

One of the main problems of the low temperature WGS reaction is a low activity of the conventional granulated CuZnAl catalyst per the unit volume of the catalyst bed due to a low loading density and a poor access of reagents into the bulk of granules due to internal diffusion limitations [1,2]. This work presents main features of design and basic characteristics of ceramometal catalysts with enhanced real and loading density possessing also a developed system of transport macropores and mesopores [3,4] .

## 2. Experimental

As starting materials aluminum powder with platelet-shaped particles, electrolytic copper powder of dendritic shape and a high purity iron powder were used. The powders were mixed in the ratio corresponding to $Al_{26}Cu_{74}$ and $Al_{36}Cu_{43}Fe_{21}$ alloys composition and mechanically milled (MA) in an APF mill (20 g acceleration) under air for 3, 6, 9 and 12 min. The details of MA procedure are presented in [3]. The procedure of porous cermets preparation from the MA product included next steps: loading of the MA product into a stainless steel die specially designed to ensure a free access of water and hydrogen release; hydrothermal treatment (HTT) of the loaded die in boiling water for few hours. This stage provides formation of strong monoliths due to conjugation of the red-ox reaction of aluminum oxidation and formation of contacts between the particles due to crystallization of aluminum hydroxides. Similar to the stage of MA, oxidation of Al at HTT stage diminishes the extent of the exothermic reaction of Me-Al interaction at the stage of calcination. Last stages include removing the monolithic product of HTT from the die followed by drying for 1 hour at 120°C and thermal treatment under air at 550°C.

The cermets before and after WGS testing were studied by XRD, SEM with an energy-dispersive spectroscopy unit EDX INCA, TPR. Compressing (crushing) strength and textural properties were also controlled. Catalytic activity of samples in the water gas shift reaction was estimated using a flow system in the temperature range of 160-270°C at atmospheric pressure. The tests were performed in the reaction mixture $CO : H_2O : H_2 = 8 : 42 : 50$ for a catalyst fraction (0.14– 0.25 mm) mixed with quartz fraction of the same particle size in 1:1 ratio as well as for a coarse fraction (3x3x5 mm). Before tests, catalysts were activated in 5% $H_2$ in He for 2 h at 270°C.

## 3. Results and discussion

It was found that cermets consist of metallic and oxide phases. The microstructure of initial cermets is comprised of the metallic phases cores randomly distributed in the oxide matrix forming oxide egg-shell (Fig.). For CuAlO/CuAl system the metallic cores consist of Cu(Al) solid solution along with $Al_2Cu$ and $Al_4Cu_9$ intermetallides, while CuFeAlO/CuFeAl ceramometals additionally contain Fe, Cu(Fe) solid solution depending upon the time of preliminary MA. The oxide shell of CuAlO/CuAl samples includes CuO, amorphous alumina and mixed Al-Cu oxides, while for CuFeAlO/CuFeAl ceramometals iron oxides are present as well. The amount of $Al_4Cu_9$ intermetallide was found to pass through the maximum at MA time 9 min. For CuFeAlO/CuFeAl samples this amount gradually diminishes with MA time. Non-monotonous variation of the specific surface area (SSA), pore volume and crushing strength with the time of preliminary MA was revealed. Correlation of specific activity with $Al_4Cu_9$ content for similar types of ceramometals was found. Catalytic activity of ceramometals in WGS reaction estimated for their fine fractions and expressed as the efficient first-order rate constant is lower than that for CuZnAl oxide catalyst due to a lower (by an order of magnitude) specific surface area of ceramometals. Specific activity of ceramometals expressed as specific rate constant related to the unit surface area of metallic copper exceeds that for CuZnAl oxide catalyst. The presence of ultramacropores with the size up to tens of microns (Fig) as well as enhanced density was shown to be typical for ceramometals, while for oxide catalysts these macropores were absent. As a result, the activity of the coarse fraction of ceramometal catalysts in WGS was higher than that of CuZnAl oxide [2]. In the average ceramometal granules possess twice as higher specific density as compared with that of ceramic catalysts. Mild leaching produces an additional increase in the activity of granulated cermets.

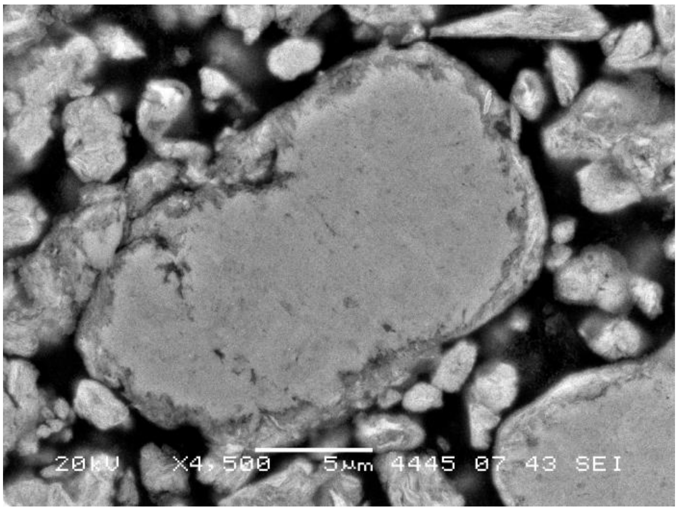

**Figure 1.** CuAlO/CuAl cermet prepared from CuAl powder (9 min of mechanical alloying).

The reasons of the difference of specific activity of surface copper and possible ways of further increase of activity of ceramometal catalysts are discussed.

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## 4. Conclusions

Design of novel porous ceramometal catalysts for low temperature WGS is described in details. Preparation procedure includes mechanical alloying of powdered metals (Cu-Al and Cu-Fe-Al), hydrothermal and thermal treatment. The variation of structural and textural properties of ceramometal catalysts with the time of MA of powdered precursors was elucidated. These catalysts demonstrate egg-shell microstructure, enhanced macroporosity and loading density, with volume activity being comparable to conventional oxide ceramic catalyst. Hence, preparation of WGS catalyst from Al-containing powders is promising for the practical application.

## References

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