METAL-CERAMIC COMPOZITES

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Abstract: Cermets belong to the composites structurally integrated, obtained from a metal or alloy (respectively from more alloys or metals) and one or more ceramic phases. The compound ratio (metal and ceramic) may vary a lot, and the cermet process runs at high temperatures, in a protection antioxidant atmosphere.

Keywords: Cermet, ceramic, alloy

1. INTRODUCTION

Modern procedure (especially the contemporary one) claims materials that, besides specific proprieties of ceramics, have good characteristics of ductility, mechanical resistance, heat conductivity, electrical conductibility etc. – specific proprieties of the metals.

Cermets, belonging to the composites, fulfil such requirements as they take from the compounds (metal and ceramic) their valuable proprieties, being suitable for the composite structure.

According to ASTM [1], there are two fundamental definitions of cermets:

- Cermet is a heterogeneous combination between metal (metals) and alloy (alloys), and one or more ceramic phases, and
- Cermet is a heterogeneous combination between a metal (metals) or alloy (alloys), and one or more ceramic phases, where the last ceramic phase represents 15-85 % (in volume), and where it occurs a feeble solubility between the two phases at the preparation temperature.

Obtaining materials having the composition of the cermets, it tries to answer some special requirements of

the modern technique, blending the characteristics of ductility, mechanical resistance, conductivity etc. – specific to the metals – with those of stability at high temperature, chemical stability – specific to a lot of ceramics.

The information concerning the effective preparation of the Al₂O₃-Cr-Mo metal-ceramic composites are little [1-171. But it considers that this material has a great importance and it is necessary for the modern technique. This importance results from their good proprieties given by cermets (anterior mentioned), and, moreover, have a good auto-lubrication when functioning at high temperatures, characteristic given by the presence of Mo and Cr- recognized having this type of proprieties. These metal-ceramic composites may be applied to the metal cutting. That is why ceramometallic composites Al₂O₃-Cr-Mo are suitable for using as drill to obtain metallic tubes. Important is also their usage for obtaining the pieces with frictional resistance (bearings, liners, balls) meant to equip the machineries and aggregates that function at high temperatures - such as energetical aggregates. The proprieties of the basic materials are shown in table 1.

Tabel 1 Potential constituents of the cermets Mo-Al₂O₃ MoSi₂-Al₂O₃, Mo-MgO, Al₂O₃ - Cr - Mo

Constituent	Thermal extension coefficient,	Melting point,				
	$(x . 10^{-6}) \text{ cm/cm.}^{0}\text{C}$	°C				
Alumina (Al ₂ O ₃)	8,8	2020				
Magnesium Oxide (MgO)	14,0	2800				
Molybdenum Disilicide (MoSi ₂)	4,5	2032				
Chrome	0,165	1900				
Molybdenum	17	2800				

Cermets are known, in general, as materials having weak internal links, sometimes characterized by the metal extrusion, which is its separation from the ceramic compound when the heat treatment occurs in the presence of the liquid phase. That is why, many times sintering treatments are applied without the melting form, even if the mechanical proprieties aren't favoured. As mentioned, cermets are composites made up of two or more phases (in different proportions) — metal part and ceramic part. In certain condition of temperature and environment a link between phases is formed, obtaining a material structural integrated.

On the one side, the proprieties of cermets depend on the ones of their compounds, and on the other side, on the proportions in which these compounds are used, and the way of their elaboration. According to the compound proportion there are the following situations [2]:

- the metal can be dispersed on a ceramic frame (when the ceramic volume is up to 60% of total volume) for instance such compositions as MgO-Ni;
- the ceramic compound can be dispersed in metal matrix (ceramic volume is lower than 40% of total volume) as in pieces (tools) with a high resistance that can be used at a greater cutting speed than to ordinary tools:
- both metal and ceramic compound can form two structures equally important, deeply bonded like in chromal $(50\%\,Al_2O_3+50\%\,Cr)$ that has a high refractoriness and resistance to heat shocks.

Cermets are made up of a rigid ceramic phase and a plastic metallic phase. Cermet resistance depends on the specific proprieties of the two phases, and the cermet structure determined by the deep arrangement between the particles of the two compounds [21].

On of the typical features of the metal-ceramic material is that its qualitative proprieties can be improved owing to modify its structure, without changing the proprieties of the phases. Increasing the continuity degree of the ceramic frame to improve the compression resistance of the cermet is a way to follow in this context.

It is known that the interface proprieties influence the cermet resistance [24] and regard particularly mechanical, electrical, geometrical proprieties of the interface metal ceram [9]. It is also known that in the sintering phase, formed at the obtaining temperature of the cermet, occurs a ceramic compound mass transfer [24]

The longer the mass transfer process of the ceramic compound, the weaker the link metal-ceram, and the cermets will have a lower resistance. This undesirable phenomenon can be stopped by following attentively the sintering treatment or by using certain chemical additives.

In general, there are two principal types of cermets: with oxide base, and with carbides, nitrides and silicides base. The main classical methods for preparing the cermets are [11-13]:

- poliphase sintering (or co-sintering), under charge or without charge;
- impregnating a porous ceramic with melted metal;
- casting under pressure
- isostatical explosion.

In every case, the cermet compounds must be chosen according to their chemical compatibility at the elaboration temperature and usage temperature of the cermet. The two phases must have a very low chemical reactivity to create good condition for metal-ceram diffusion, then forming an intermediate zone between particles. Another condition is to establish a protection atmosphere to avoid the metal oxidation. Besides, the chemical compound must be stable; a condition imposed is that the metal electropositive character be much less than that of the ceramic compound cation [14].

Basic materials

The metal-ceramic composites like Al_2O_3 -Cr-Mo are materials that use as basic compounds molybdenum (Mo), chromium (Cr) and alumina (Al_2O_3), and those like $MoSi_2 - Al_2O_3$ use molybdenum disilicide ($MoSi_2$) and alumina (Al_2O_3).

The metallic compound may be a semi finished material like $MoSi_2$ – an intermetallic compound also obtained after a heat treatment in protective atmosphere, in the most cases argon atmosphere, by a synthesis reaction where molybdenum and silica or their compounds (salts, oxides, etc.) are basic materials.

Ceramics as basic materials

Al₂O₃. (Alumina) sintered is obtained after certain complex chemical and heat treatment processes, starting from divers aluminium derivates. According to the heat

treatment temperature, and the way that this process is run, aluminium oxide has different reactivity degrees. Sintered alumina has a lot of utilizations, such as preparing ceramics and refractory, abrasives, composites (cermets like $Mo-Al_2O_3$, $MoSi_2-Al_2O_3$ etc), electronic pipes etc. $\square\alpha-Al_2O_3$, being stable at high temperature, is the one form used for obtaining ceramo-metallic materials.

Metals as basic materials

Metals, alloys or inter-metallic compounds must be used as very fine powders to the preparation of the cermets (2- 5μ) [18]. The metals powders are obtained by powder metallurgy or by an advanced grinding.

Molybdenum is a transitional element, positioned in period V and group VI within periodic system of elements, has the atomic number 42, and the atomic mass 95,94. Molybdenum has the specific weight 10,2 g/cm³, melting point at 2620°C, and boiling point at 3700°C.

Molybdenum, with the particles of 325 meshes and a uniform grain size, is a suitable material to start the elaboration of the cermets $Mo-Al_2O_3$

It must be mentioned that also the grain size of the metallic powders have, usually, values on a narrow range by contrast with ceramics. This influences directly the phase formation and distribution in the final product. If it doesn't care about the grain size, it can be obtained inelastic composites having a fragile behaviour [19].

Chromium (Cr) is a metallic chemical element. A white bright metal, density 7,2 [kg/dm3], melting point at 1 890° C, boiling point at 2480° C. As pure metal, it is malleable, ductile and tenacious.

Chromium is a white bright metal and it crystallizes in cubic system with centred volume, without other allotropic forms. It is malleable, ductile and tenacious, having a high fusibility.

Molybdenum disilicide (MoSi₂) is an intemetallic compound synthetically obtained, in certain conditions, from its metals (molybdenum and silica) or from the chemical compounds of these metals (salts, oxides etc) [20-23]. The main method, where molybdenum disilicide is obtained for industry domain, is from molybdenum and silica.

To realize a cermet, it must be taken in account a lot of criteria. One of them considers necessary the existence of a similitude between the curves dilatation-contracting, according to the temperature of the cermet constituents. That supposes the compound sintering to begin in the same short temperature interval and to be carried out with comparable kinetics, that the sintering of one phase not to be disturbed by the other inertia.

3. OPTAINING THE COMPOZITES $Cr - M_0 - A1_2O_3$

It was used the following basic materials to obtain this composite: metal phase -30% Cr : 15%, Mo : 15% and ceramic phase -70% - reactive alumina.

It was used isopropyl alcohol as wet agent, 40% by rapport of dry mass, prepared in the dosage conditions mentioned to realize a deep composite, in crude form. The deep mixture of the two compounds (cermet constituents), dried in the way presented above, was pressed in a mould with punch at a pressure of min. 10 MPa. The shaped pieces had a cylindrical form with $\Phi = H = 20$ mm.

The pieces mentioned above were heat treated at 1450°C in a graphite resistance oven, into an argon atmosphere (at a pressure of 0,3 atm over the air pressure). The protection atmosphere prevents the oxidation process of the metallic compounds during their heat treatment.

The chemical composition and the size of metallic reactants used in the experimental works are shown in the tables 2 and 3, and the rontgenografical analysis of alumina is presented in figure 1.

Table 2. Chemical composition of the reactants

Reactant elements	Elementary chemical composition, %									
Molybdenum powder	Mo	Si	S	Fe	C	Mg	Ca	Mn	Cu	Al
(Merck)	Base	traces	0,75	0,16	0,09	0,75	1,86	0,53	< 0,05	-
Chromium powder		•	•	•	Over 9	9,5 %	•	•	•	
(Merck)										

Table 3. Reactant grain size in powders

Tuble of Redectant grain size in powders					
Base material	Rest on the strainer seen with free eye (mm)				
	0,4	0,2	0,09	0,06	< 0,06
Molybdenum powder (Merck)	1,2	2,4	2,4	3,0	91
Chromium powder (Merck)	0,5	1,4	62,3	21,0	14,8
Alumina Martinswerk	-	-	-	-	100

Table 4. Properties of the cermets, studi at 1450 °C

Apparent density, g/cm3	4,78
Absorption, %	2,9
Mechanical resistance, daN/cm2	>1420
Heat shock resistance 20 – 1200°C	>20
Oxidation resistance expressed by increasing the	0,0015
weigh at 1200°C for 96 hours, g/cm3	
Hardness	340 HB

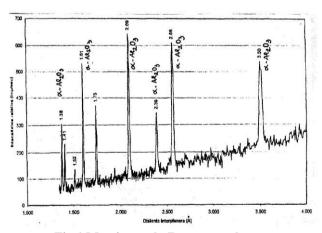


Fig.1 Martinswerk Roentgenogharm

When using the Molybdenum and chromium fine powders to obtain the ceramometal studied, the characteristics of the final product showed (table 4) that the cermet process was run at $1450^{\circ}C$.

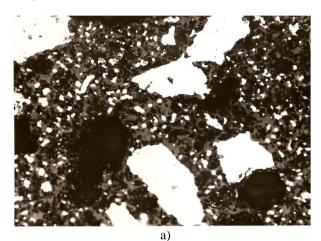
The studied composition has, in such conditions, mechanical resistance, heat shock resistance, chemical resistance (also corrosion resistance) and a very good hardness, specific to cermets, aspects proving that the process of forming the links metal-ceram was for 1450°C. The electron microscopic study of the composites supports the affirmations presented above as regards the cermet process of the system Al₂O₃-Cr-Mo. The images shown in the figure 1 a, b, prove that there aren't micro cracks on the shaping surface of the cermets, being a further prove that the cermet process was run at the treatment temperature in a protective medium (nitrogen at a pressure of 0.3 atm greater than air pressure).

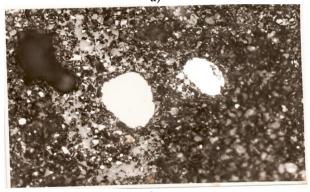
From data obtained from the material study after cermet process, it can conclude that this cermet process in the system studied is finished at 1450°C.

7. CONCLUSIONS

- Studying a large bibliography, it was carried out the experiment having as target the obtaining of the metal ceram composites with high proprieties.

- After previous trials that focused the highlighting of the forming process initiation for the links metal-ceram, the cermet process was followed at $1450\,^{\circ}\text{C}$.
- Apparent densities has high values (4,78 g/cm³⁾.
- Applying different research methods, such as mechanical, physical and chemical methods over the studied compositions, it found out that these materials had mechanical resistance at heat chock, chemical resistance (corrosion resistance) and hardness, characteristic for the cermets.
- The electron microscopic study of the composites shows that there aren't micro cracks on the shaping surface of the cermets, being a further prove that the cermet process was carried out at the studied treatment temperatures.





b)
Fig 2. a,b cermet $Al_2O_3 - Cr - Mo$ obtained at 1450 °C x 1200

8. REFERENCES

- [1] J. A. Voigt, D. L. Sipola, K. G. Ewsuk, B. A. Tuttle, R. H. Moore, T. V. Montoya, and M. A. Anderson, "Solution Synthesis and Processing of PZT Materials for Neutron Generator Applications," SAND98-2750, December 1998;
- [2] S. J. Glass, E. K. Beauchamp, S. L. Monroe, J. J. Stephens, R. H. Moore, J. P. Brainard, K. G Ewsuk, E L. Hoffman, R. E. Loehman, G. A .Pressly, and J. E. Smugeresky "Mo- Al2O3 Cermet Research and Development," SAND97-1894, August 1997;
- [3] J. A. Voigt, S. J. Lockwood, R. H. Moore, P. Yang, B. A. Tuttle, "PZT 95/5 for High Energy Density Applications: Synthesis, Processing, and Properties," 104th Annual

- Meeting of the American Ceramic Society; St. Louis, MO; Apr. 2002;
- [4] D. L. Sipola, J. A. Voigt, S. J. Lockwood, and E. D. Rodman-Gonzales, "Chem-Prep PZT 95/5 for Neutron Generator Applications: Particle Size Distribution Comparison of Development and Production-Scale Powders," SAND2002-2065, July 2002;
- [5] S. J. Lockwood, E. D. Rodman, S. M. Deninno, J. A. Voigt, and D. L. Moore, "Chem-Prep PZT 95/5 for Neutron Generator Applications: Production Scaleup Early History," SAND2003-0943, March 2003;
- [6] V. Teixeira, E. Sousa, M.F. Costa, C. Nunes, L. Rosa, M.J. Carvalho, M. Collares-Pereira, E. Roman, J. Gago. "Spectrally selective composite coatings of Cr-Cr2O3 and Mo-Al2O3 for solar energy applications", Thin Solid Films, 392, p. 320-326, 2001;
- [7] Huffadine, J.B. Special Ceramics, Heywood and Company LTD, Londra, 1960;
- [8] Shevlin, T., S. Proc. CERMETS, Reinhold Publishing Corporation, New York, 97, 1960;
- [9] Mishnaevsky, L., L. Proc. 4 th Int. Symp. On Brittle Matrix Composites Woodhead Publishing Ltd., Abington Cambridge, 1994;
- [10] King, W., E. Mater. Sci. and Engineering, A 191, 1 16, 1995;
- [11] Mishnaevsky, L., L. Pro. 4 th EURO- CERAMICS, Vol. 4, 379, Faenza – Italia, 1995;
- [12] Angelescu, N. Materiale compozite cu fază ceramică. Editura Științifică F.M.R., Bucureşti, ISBN: 973-8151-37-6, pp. 1 – 284, 2005;
- [13] Oprea, F., Angelescu, N. Bisiliciura de molibden material cu proprietăți anticorosive şi rezistive. Editura Macarie, Târgovişte, ISBN 973-8135-93-6, pp. 1-185, 2002;
- [14] Angelescu, N. s.a. Considerații privind sinteza MoSi₂ şi obținerea compozitelor ceramometalice cu fază ceramică din alumină rezistente la coroziune. Revista de Chimie, 58, Nr. 12, 1239-1243, 2007;
 [15] Angelescu, N. Some Considerations Regarding MoSi₂ Synthesis. Ceramics International, 24(1), pp. 73-76, 1998, ISSN 0272-8842;
- [16] Angelescu, N. MoSi₂ Al₂O₃ Cermet Type. Seventh ECERS, Brugge, Belgium, 2001 (Publicat in 2002). Key Engineering Materials, Trans Tech Publications, Switzerland • Germany • UK • USA, Vols. 206-213, pp. 665-668, ISBN 0-87849-882-6, 2002;
- [17] Oprea, F., Angelescu, N. MoSi₂ Self Purification through High – Temperature Synthesis. The 5th European Ceramic Society Conference. Key Engineering Materials, Trans. Tech. Publications, Switzerland, Vols. 132-136, pp. 806 – 809, 1997.
- [18] Mishnaevsky, L., L. Proc. 4 th Int. Symp. on Brittle Matrix Composites Woodhead Publishing Ltd., Abington Cambridge, 1994.
- [19] Kingery, W., D. Introduction into Ceramics, Wiley, New York, 1960.
- [20] Weber, C., B. Proc. CERMETS, Reinhold Publishing Corporation, New York, 58, 1960.
- [21] Goetzel, C. Proc. CERMETS, Reinhold Publishing Corporation, New York, 73, 1960.
- [22] Wambold, J. Proc. CERMETS, ReinholdPublishing Corporation, New York, 86, 1960.
- [23] HufFadine, J.B. Special Ceramics, Heywood and Company LTD. Londra, 1960.
 [24] Shevlin, T., S. CERMETS, Reinhold Publishing Corporation, New York, 97, 1960.