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Journal of the European Ceramic Society 25 (2005) 1049–1055
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Testing strategies for corrosive interactions of ceramics with semi-solid and molten metal alloys

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Received 27 February 2004; accepted 1 May 2004
Available online 13 July 2004

Abstract

For the suitability assessment of ceramics or refractory materials for tools, crucibles or handling aids in metallurgy and metals processing, e.g., for thixoforming or rheocasting, besides properties such as wetting behaviour, wear resistance, thermal conductivity and thermal shock resistance, mainly the corrosion behaviour against the processed alloy influences the service life of a tool material. This paper presents a testing strategy to characterise the corrosion properties.

Keywords: Refractories; Testing; Corrosion; Alloys

1. Introduction

Ceramic materials have a high potential for use in metallurgy and metals processing because of the excellent high-temperature properties, strength and wear resistance. They may withstand under many conditions whereas metal materials fail relatively soon. Nevertheless not all applications of ceramic materials in contact with metals and metal melts have been exploited yet by far. This is mainly due to information deficiencies by the industrial users concerning the different types of ceramics, their characteristic properties and resulting possible fields of application, but in many cases also based on too high expectations regarding technical feasibility, limitations in mechanical properties and design, precision in shape, and reproducibility of manufacturing.

The requirements on ceramic components within the above-mentioned fields of application are numerous and often very complex. They include mechanical, chemical, thermal and tribological loads which mostly occur at the same time. Often it is not possible to simulate such a complex load environment by one model test only. Rather various tests procedures must then be applied subsequently which may yield different results compared to the combined load in an industrial use. Thus, the development of novel model tests should not be neglected.

Especially in the field of metal forming the shape accuracy of tools and die materials is very important. Only small variations in cavity dimensions and surface quality may lead to the rejection of the product. Therefore, besides temperature and wear resistance, first of all the resistance against corrosive attack by the alloys to be moulded as well as by the scale layers or slags plays an important role decisive for the life time of thixoforming tools. By this relatively novel forming technology an alloy is processed in the range between solidus and liquidus temperature, and therefore, is just partly molten. There are only few experiences concerning interaction effects of different ceramic tool materials with semi-solid alloys and scales. For thixoforming of copper alloys and steels the tool material problem is one of the main facts which are limiting a wide industrial implementation up to now.[1,2]

This paper focuses on chemical-corrosive load of ceramic and refractory materials in contact with metals at high temperatures. This load case is classified very critical, because a chemical reaction of the component with its environment may affect the functionality seriously, whereas thermo-mechanical properties such as, e.g., thermal shock resistance or high-temperature strength are adaptable to the demands within certain limitations by a suitable microstructural development or an adequate process control.

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doi:10.1016/j.jeurceramsoc.2004.05.005

The main goal of this work is the development and optimisation of appropriate model tests. A fast examination procedure is presented, which enables an overview on corrosive reactions of technical ceramics and refractory materials with aluminium, copper and steel alloys. All melt and contact corrosion tests have been carried out with most commercial and some especially developed ceramics and composite ceramics. Six different alloys were treated: aluminium wrought alloy AlMgSi1, aluminium cast alloy AlSi7Mg0.3, bronze CuSn8 or CuSn6, respectively, brass CuZn37, ledeburitic high-speed steel HS6-5-2 (M2 tool steel), and ledeburitic steel 16MnCrS5.

2. Melt corrosion

2.1. Development of experimental set-up

Melt corrosion tests (rod tests) have been performed with ceramic rods ("fingers") first of all in a Tammann furnace (Figs. 1 and 2). This type of furnace is resistance-heated by a graphite heating tube and can be fired up to 2100 °C. Due to the graphite shroud and the use of protecting gas Ar4.6 (99.996% argon) the experiments take place in reducing atmosphere. The ceramic sample is fixed to an Al_2O_3-tube by a ceramic cement and connected by a steel clamping to a motor for sample rotation with 30 rpm. The interior of the furnace is covered by a two-part top made of refractory material. This furnace is convenient especially for alloys which tend to oxidise and to produce a scale layer on the melt surface.

Due to the relatively fast thermal wear of protecting and heating tubes and the lack of variable sample movement a specially designed melt corrosion furnace has been developed (Fig. 3). This custom-made unit is equipped with $MoSi_2$ heating elements and thus enables tests up to 1750 °C

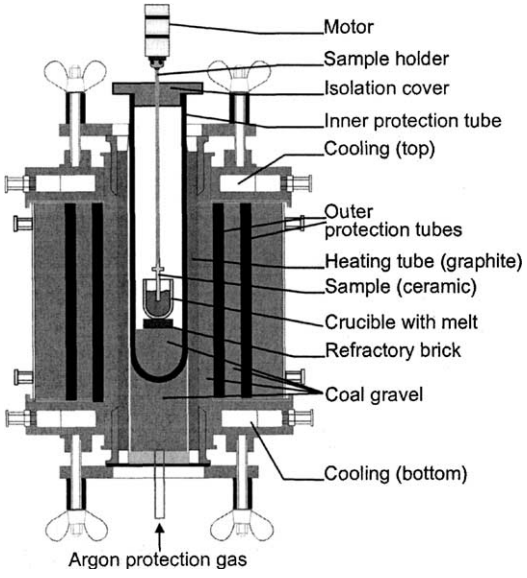

Fig. 1. Tammann furnace for melt corrosion.

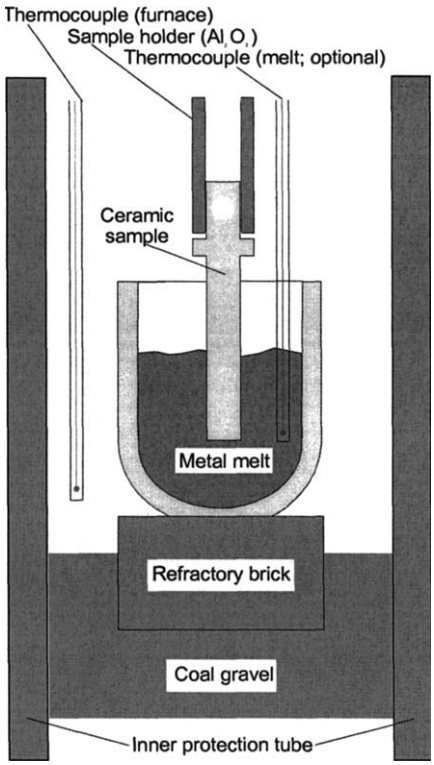

Fig. 2. Experimental set-up (rod test).

in air and different protecting flush gases. Dependent upon the furnace insulation material its use up to 1850 °C is possible, too. Temperature control and sample movement can be programmed independently from each other. The sample can be rotated left and right with up to 62 rpm and submerged alternately (lifting speed 2 m/s). Besides the thermocouple for furnace control a second thermocouple is placed under the melt crucible to record the melting of the alloy.

2.2. Materials preparation and test procedure

The alloys are sawed to suitable size, degreased and filled into a crucible made of 99.7% Al_2O_3. The ceramic samples are used either in finger shape (green machined and sintered) with non-treated surface or are cut out from large pieces and ground. They also can be polished like bending test bars. After preparation the samples are fixed to the sample holder by a high-temperature resistant ceramic cement based on water glass (Na-/K-silicates). This joint first hardens overnight (hydraulic binding), but maximum strength is reached only during heating-up in the furnace (ceramic binding).

To avoid thermal shock the ceramic samples are heated up together with the alloy inside the furnace. After melting of the alloy the sample is submerged to the melt for 15 min up to 24 h depending on the alloy. The target temperature is adapted to the processing temperature of the alloy or ranges between 50 and 100 K above the melting temperature. Each test requires a new crucible to minimise impurities of the melt (Table 1).

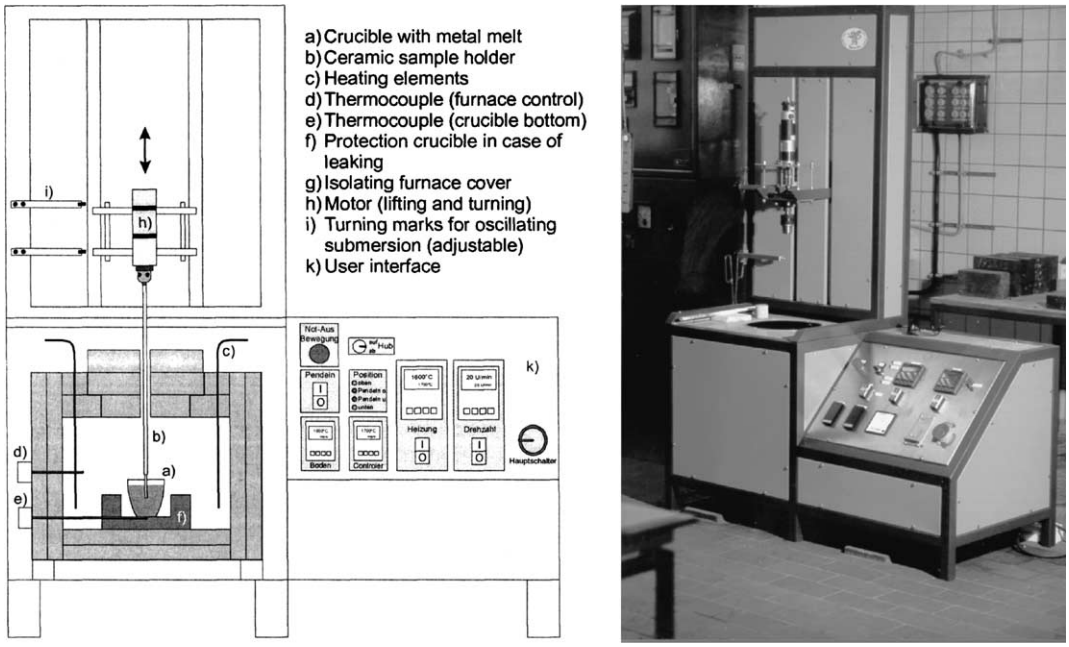

Fig. 3. Specially developed melt corrosion equipment.

Table 1
Examples of testing parameters melt corrosion (TF: Tammann furnace; MCF: melt corrosion furnace; Ar4.6: protecting gas 99.996% Argon)

Alloy	AlSi7Mg0.3	CuSn6	HS6-5-2 (M2 tool steel)
Input (g)	800	600	600
Heating rate (K/min)	10–15	10–15	15
Target temperature (°C)	740	1100	1470
Test duration	8, 12, 24 h	50 min–6 h	1 h
Melt additives	Refinement salt; none	None	None
Furnace type	TF, MCF	TF, MCF	MCF
Atmosphere	Reduced, air	Reduced, Ar4.6	Ar4.6

3. Contact corrosion

For studies of corrosion behaviour of ceramic materials in contact with semi-solid alloys the contact corrosion test was developed as a model testing procedure being uncommon up to now. Melt corrosion testing with a partly molten alloy would be hardly feasible due to the narrow temperature range to be kept for the desired fraction of liquid. Therefore, temperature control has to be very accurate. There is a high risk of the melt becoming too viscous, not keeping a continuous contact with the sample (stirring hole formation) or spontaneous freezing. This would result in rupture of the sample holder and damage of furnace interior or thermocouples.

For contact corrosion with semi-solid alloys the samples are used in a sandwich arrangement resembling ceramic–metal–ceramic diffusion couples. The advantage is the possibility to study chemical-corrosive interactions between ceramic material, solid and liquid metal as well as scale of the alloy simultaneously. Furthermore, testing may be carried out within real processing temperature interval (solidus–liquidus interval).

3.1. Development of experimental set-up

The optimum experimental set-up has been selected from different sample holder concepts (Figs. 4–7). A special sample holder made of refractory concrete was most favourable since this allows an individual load of 0.5–1.0 MPa to be placed onto every sample depending on the sample size (Fig. 7). Eight sandwich samples can be heated to target temperature at the same time. The alloy slugs soften and are compressed by the load. By this effect the contact between

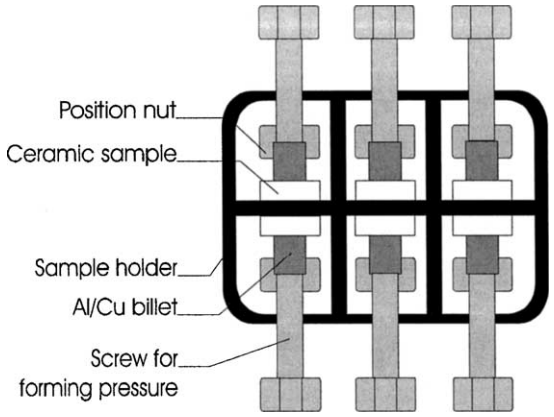

Fig. 4. Contact corrosion holder made of steel with pressure load by screws (set-up 1). No pressure load after softening of alloy slugs, not oxidation resistant.

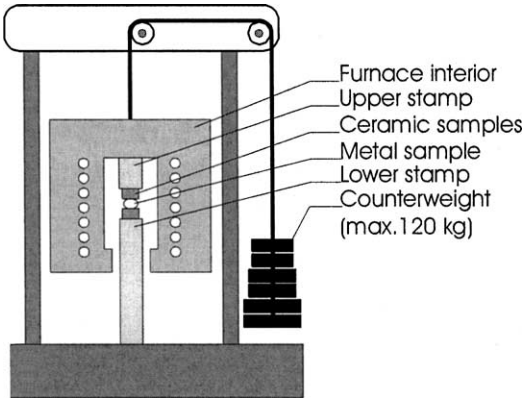

Fig. 5. Contact corrosion in a long time creep testing equipment (set-up 3). High testing expenditure, only one sample per test.

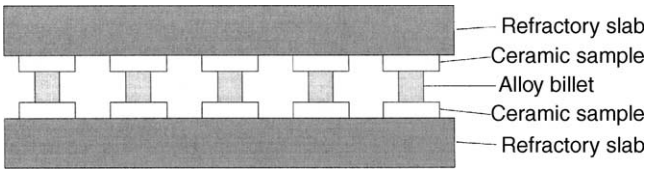

Fig. 6. Contact corrosion with pressure load by a refractory sillimanite sheet (set-up 2). No regular distributed individual load after softening of alloy slugs.

ceramic and metal material or semi-solid melt is improved. At the same time a part of the scale sticking on the alloy is pressed against the ceramic surface, too. Thus, interaction effects with metal as well as with scale can be included in the examinations.

To consider the influence of atmosphere, the tests took place in air and reducing protecting gas atmosphere (Ar or Ar–H_2). For the tests in protecting gas atmosphere a similar construction is used fitted into a gastight protecting tube made of Al_2O_3 which is closed by a water-cooled flange and can be flushed with different gases (Figs. 8 and 9).

3.2. Materials preparation and test procedure

The alloys are used as parallely ground or turned cubes (5 mm × 5 mm × 10 mm) or 10 mm high cylinders with 8 mm of diameter. Ceramic samples are smoothened, too, measuring 5 mm × 15 mm × 15 mm. The cleaned samples are inserted into the sample holder (sandwich arrangement: ceramic–metal–ceramic), and the load is applied. The sample holder is set into the furnace and heated up with constant heating rate to processing temperature. At the end of testing time the furnace cools down freely (Table 2).

For selection of materials for thixoforming tools a target temperature between solidus and liquidus temperature of the alloy is chosen. The processing temperature depends on the desired fraction of liquid (usually between 40 and 80 vol.%). It can be either taken from phase diagrams or from time–temperature–transformation diagrams. It has to be taken into account, that the increase of fraction liquid with temperature often is non-linear.

4. Evaluation methods

At the end of testing time and cooling down the corrosion samples first are inspected macroscopically for deformation, coloration, and obvious phase boundaries. Fig. 10 shows a case of an arrangement of non-wetting boron nitride in contact to steel.

The sample is then imbedded in a two-component resin, prepared ceramographically in cross section (diamond precision saw, diamond polish down to 1 μm grit size). Figs. 11 and 12 present examples of as-cut and polished sandwich samples of steel in contact to alumina, respectively. After cleaning in an ultrasonic bath the section is examined by reflected light microscopy (in polarised and non-polarised light) as well as by scanning electron microscope (SEM) with electron dispersive X-ray analysis (EDX). Besides, for selected samples X-ray diffraction analyses (XRD) were made. The evaluations are supplemented by thermo-chemical equilibrium calculations.

Regarding ceramics with translucent crystallites the polarization unit of the reflected light microscope enables infiltration zones to become visible. The vertically reflected light can be faded out and only the light reflected by inclining grain and phase boundaries beneath the surface becomes visible. This technique is called “scattered light method”. In case of yttria-stabilised zirconia in contact to steel dendritic precipitates of iron oxide become visible beneath the

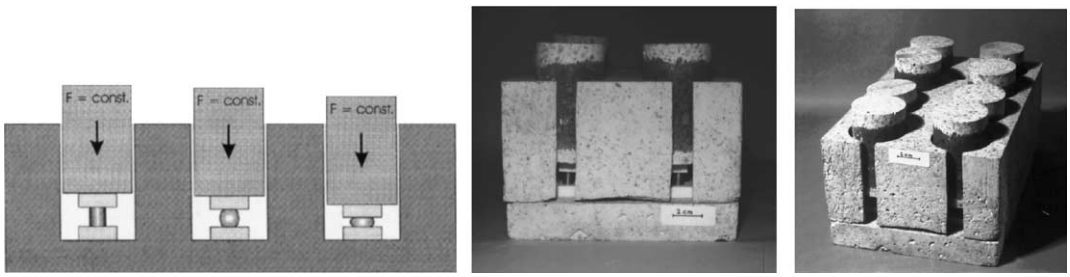

Fig. 7. Contact corrosion sample holder (refractory concrete) with sandwich sample arrangement (ceramic-metal slug-ceramic diffusion couples, set-up 4). Optimum single loading, testing of up to eight samples under same conditions possible.

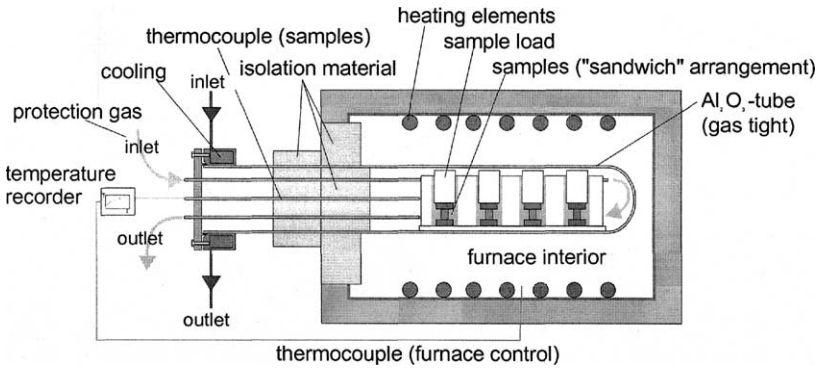

Fig. 8. Contact corrosion test in protecting gas atmosphere: experimental set-up (set-up 5).

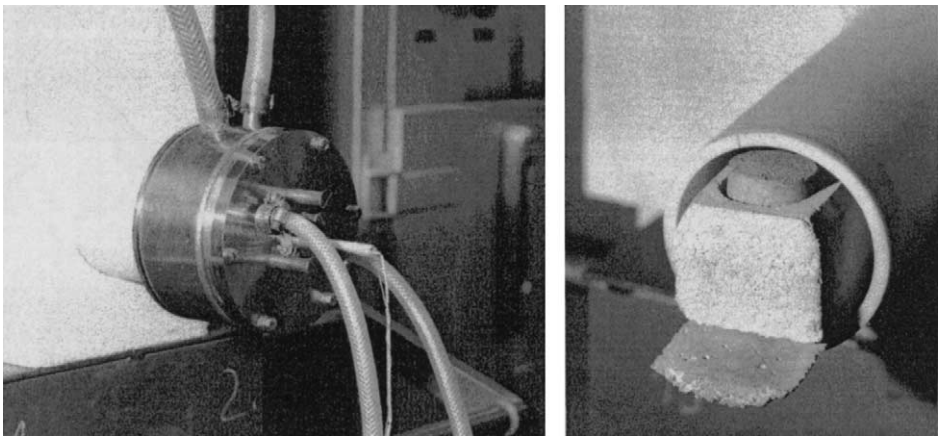

Fig. 9. Contact corrosion test in protecting gas atmosphere: water cooled flange (left), adapted sample holder in Al_2O_3 tube (right) (set-up 5).

surface of the ceramic which are due to continuous diffusion from the contact area into the ceramic (Fig. 13). Local supersaturation of the solid solubility of iron oxide in zirconia then may give rise to crystallisation. Reflected light microscopy is also recommended if small contrasts in coloration due to changes in oxidation state or small gradients in porosity have to be recognised (Fig. 14).

SEM examination is carried out on polished samples. Carbon sputtering is necessary if the samples are not electrically conducting. Mainly back scattered electrons are used to investigate changes in peripheral areas, structure, and phase modifications or formation of reaction layers in the contact zones. Fig. 15 presents a SEM micrograph of the same sample as shown in Fig. 13 but closer to the steel contact (top). Composition of phases and enrichment of elements can be specified by EDX. It has to be taken into account, that EDX analyses of phases of small particle size are often influenced by the surrounding material. In this case the subtraction of the results of the matrix composition from those of the small particles can be helpful. XRD analyses of bulk material should be carried out using samples with a minimum surface of 5 mm × 5 mm. Measuring errors may occur due to different grain sizes, packing densities or texture effects. Like EDX analyses also XRD analyses may be erroneous if the area of interest is too small. Furthermore it should be noted that XRD is a semi-quantitative method.

Thermo-chemical calculations are very useful to verify the reactions recognised by experiments. Data input is the starting composition of ceramic and metal as well as of atmosphere and the target temperature. The results include

Table 2
Testing parameters for contact corrosion tests (SU1: set-up 1, etc.; *h*: height)

Alloy	AlMgSi1	CuSn8	CuZn37	HS8-5-2 (M2 steel)	16MnCrS5
Sample geometry	∅: 8 mm, *h*: 10 mm	∅: 8 mm, *h*: 10 mm	∅: 8 mm, *h*: 10 mm	5 mm × 5 mm × 10 mm	5 mm × 5 mm × 10 mm
Heating rate (K/min)	8	8	8	8	8
Target temperature (°C)	600	900/950	950	1330/1335	1480
Test duration (h)	6	2, 6	6	0.5, 2	2
Experimental set-up	SU1	SU2, SU4, SU5	SU1	SU4, SU5	SU3, SU4, SU5
Atmosphere	Air	Air, Ar–H_2	Air	Air, Ar–H_2	Air

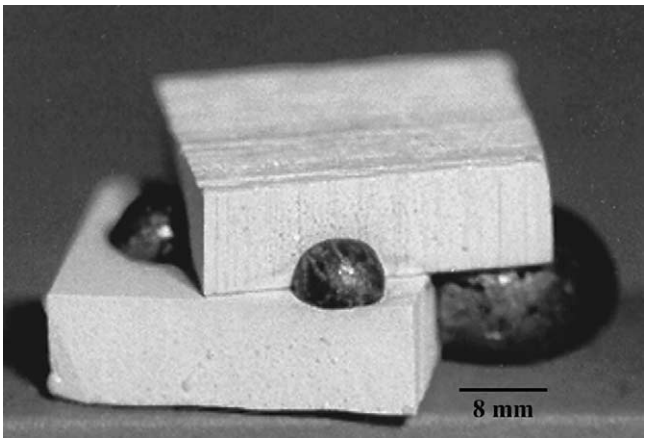

Fig. 10. As-treated sandwich sample of hexagonal boron nitride and HS6-5-2 treated at 1335 °C/2 h in Ar–5%H_2. Note that the liquid metal did not wet the ceramic but was squeezed out by the load.

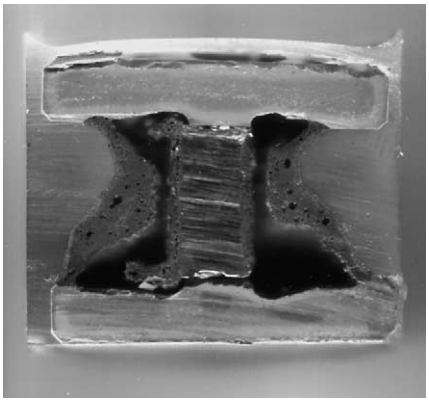

Fig. 11. Example of an as-cut sandwich sample consisting of alumina (upper part, bottom), slag right and left, and steel (inside). Height about 20 mm.

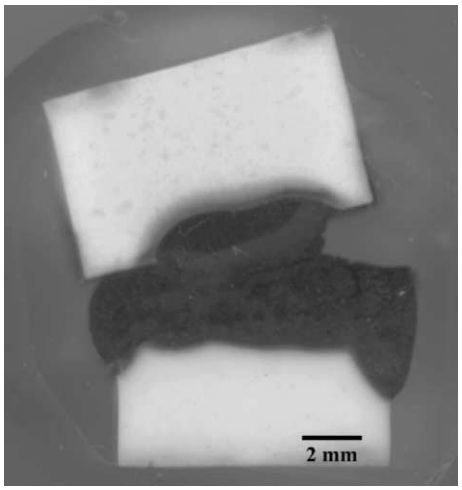

Fig. 12. Sample with strong interaction: Al_2O_3/16MnCrS5 treated at 1480 °C/2 h in air. Note that all metal was corroded to scale.

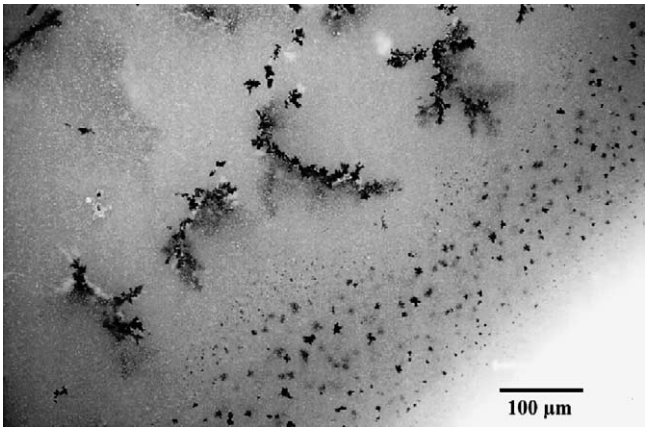

Fig. 13. Iron oxide precipitates from contact area to steel into zirconia ceramic. Note the unaffected ceramic area down right (white).

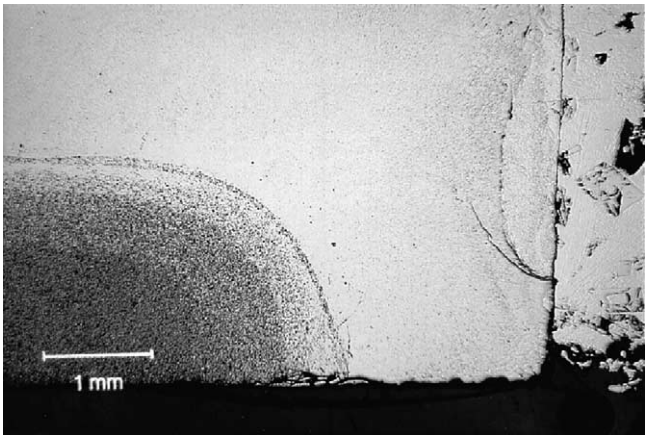

Fig. 14. Reflected light micrograph of zone structures due to variation of porosity in TiB_2–WB_2–CrB_2 ceramic in contact to HS6-5-2 after treating 1335 °C/2h in Ar–5%H_2.

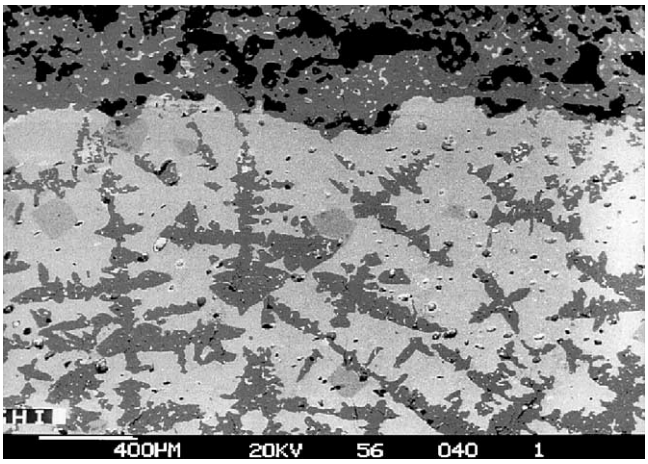

Fig. 15. Iron oxide dendrites in zirconia close to the contact to corroded steel (top).

usually only condensed phases (solid or liquid) but in some cases also the vapour phase may be of interest in particular if reaction products are volatile. To simulate the contact surface between solid ceramic and metal samples a model assumption is used: The starting components are given as an equimolar mixture (ceramic:metal = 1:1) being ideally dispersed and are allowed to react with each other for an infinite time until an equilibrium is obtained. For reactions in protecting gas atmosphere the oxygen partial pressure should be set to 2×10^{-20} bar to suppress calculation of metal oxidation in accordance to the experiments, where no significant metal oxidation occurred. The interpretation of the results has, however, to consider some restrictions. They indicate which possible reactions may be observed but do not inevitably have to take place. Usually, under the given experimental conditions, it cannot be expected that a thermodynamic equilibrium will be obtained. In particular the formation of glassy phases cannot be readily calculated although many data for slags are available already. Beyond the used model assumption which reproduces conditions at the phase boundaries only inaccurately neither impurities nor kinetic effects, gradients of element concentration or the formation of protecting layers are taken into account. Furthermore, some thermodynamic data for possible reaction products are not available. The validity of the data has to be considered, too (e.g., solubility limits). Some case studies are published in.[3,4]

5. Conclusions

The combination of examination and evaluation methods introduced by this paper offers an helpful tool for assessment of suitability of ceramics for specific applications in metallurgy and metals processing. By evaluation of ceramographically prepared samples and by support of thermo-chemical calculations the observed corrosion effects can be explained and abstracted in the form of typical reaction patterns. Damage mechanisms can be established and the ceramic materials can be compared with each other or validated concerning requirements of practice. Conclusions can also be drawn to understand adhesion problems and mechanical stability as well as to optimise additives and compounds or to choose suitable components for composite ceramics. Some results of the tests performed are presented in detail in[5–7] and will be subject for further publications.

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