Mechanical Characteristics of YSZ-based Thin-Film Coatings Obtained by Physical Sputtering in Vacuum

S.A. Sobko, Yu.G. Smirnov, V.A. Kulikov, A.P. Tkachenko

FSUE RFNC-VNIITF, Vasil'ev Str.13, Snezhinsk, 456770, Russia.
Fax: +735146-55534, E-mail: avva@ted.ch70.chel.su

Abstract – The objective of this work was to develop efficient and simple techniques for micromechanical tests of thin-film coatings on the model substrates and to assess strength and brittle fracture resistance of YSZ-based SOFC electrolytes, obtained by sputtering of the ceramic and metal targets in vacuum.

Therefore the opportunities and results of two techniques for evaluation of the mechanical characteristics of the coatings are considered: indentation, with calculation of standard and integrated micro-hardness and scratching techniques.

Tests of the coatings using the developed techniques showed the obvious advantages of YSZ-based composition coatings in the sphere of higher strength properties and fracture toughness as well.

1. Introduction

The oxide thin-film electrolytes, considered for solid oxide fuel cells (SOFC) in the long term, have some specific features: low plasticity, oxides brittleness at small thickness (about ten microns). At the same time they should be tight, have good cohesion and adhesion to the supporting substrate, even at different CTE values.

Currently there is some interest to the techniques of the surface micromechanical tests (MMT) of various materials, in particular, ceramic and composite materials.

However, for thin-film coatings, direct application and objectivity of MMT techniques are greatly limited both by the effect of the substrate and small thickness of the coatings.

2. The Goal

The goal of this work was to develop the basic techniques of MMT of SOFC thin-film electrolytes on the model substrates and to evaluate the toughness and resistance to brittle fracture of YSZ-based coatings, obtained by sputtering of the ceramic and metal targets in vacuum.

Experimental

The work considered the capabilities of two techniques for evaluation of micromechanical properties of the coatings: indentation with calculation of integral micro-hardness and scratching techniques.

1. The essence of the first technique is the following. The total hardness of the surface layer (any coating), differing in terms of the mechanical properties from the basis (substrate), depending on the indentation depth and thickness of the layer (coating) will be a variable.

Therefore model dependence of integral microhardness on the indentation depth can be the basis for evaluation of the strength properties of both the coatings and the whole "coating – substrate" system.

So integral microhardness HVJi (Pi) for the set $P_1 \ldots P_n$ interval of loadings with the specified step is calculated by formulas:

$$HVJ_n(P_n) = \frac{\sum_{i=1}^{n}[HV_i \cdot (P_i - P_{i-1})]}{P_n - P_1} \qquad (1)$$

or

$$HVJ_n(P_n) = \frac{\int_{P_1}^{P_n} HV(P)dP}{P_n - P_1}. \qquad (2)$$

This approach also allows evaluation of the loading influence on coating fracture initiation (cohesion and adhesion) in the indentation zone.

2. The main principles of ref. [1] are used in the applied scratching method. In this case the researches concerned the evaluation of influence of the set interval of indentation loadings on width of the coating straining zone (cohesion) and its separation from the substrates (adhesion).

Characteristics of Tested Samples

Metal substrates of nickel were used as tested samples. Thin-film coatings were deposited on these substrates by electron beam sputtering of ceramic and metal targets (YSZ and Ni) in vacuum. Tests were performed on one-layer coatings: YSZ and YSZ+Ni composite.

The model ceramic substrates were also coated with sputtered samples during one installation for evaluation of the structure and composition of the coatings.

The results of studying of the coatings of the surface and fractures of the ceramic substrates by XRD and micro-XRD techniques demonstrated (fig. 1), that:

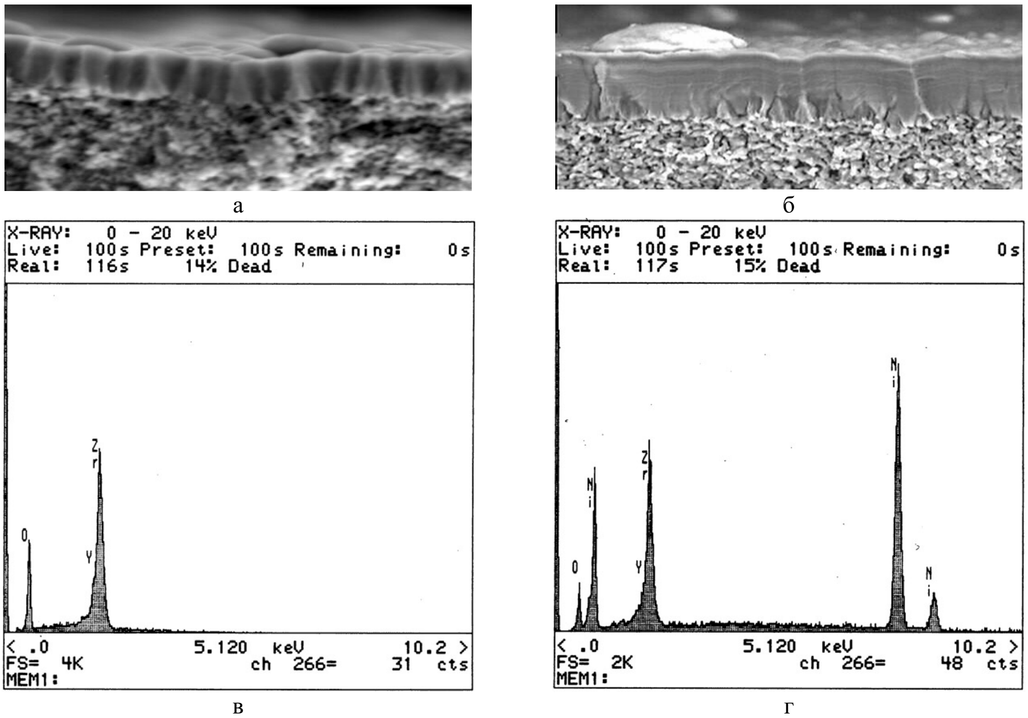


Fig. 1. Microphoto of the sample fracture and X-ray spectrum from the coating: a, c is YSZ coating, b, c is YSZ+Ni coating

1. The chemical and phase composition of coatings is exactly the same as of targets.
2. YSZ coating is porousless with clearly seen column structure.
3. The coating modified by nickel differs in its top part by dense, layered structure more typical for galvanic depositions.

Test Results

Testing setup and parameters were the following:

1. Standard certified micro-hardness meter PMT-3 was used as the testing tool
2. Test loadings P for each sample with the coating were set in the range of 0.1–2.0 N.
3. Average values of characteristics were used for construction of HV (h), HVJ (h) and l (P), L (P) curves, where h is the depth of indentation; l is the length of indentation diagonal; L is the length of fracture zone along indentation diagonal.
4. Critical parameters of formation of the coating brittle fracture initiation zone: the typical dimension of fracture initiation zone P_{cr} and the loading corresponding to this zone P_{cr} [2] were determined by the bifurcation point of two model curves l (P) and L (P).

The results of the integral microhardness calculations (fig. 2) demonstrated that integral HVJ curves of samples with YSZ coatings were consistently descending with penetration depth increase. It is associated both with the reduced strength of the grain boundaries at column-like structure of YSZ coating, and with the effect of the more soft substrate in "coating – substrate" system.

Composite coatings YSZ+Ni (fig. 3) are characterized by HV and HVJ maximal microhardness, exceeding microhardness of unalloyed YSZ coatings and reaching 12.5 GPa. Such coating is characterized by the absence of the fracture zone around indentations that is by noticeable plasticizing effect from additional alloying by the metal component.

The scratching procedures included the following:

1. Tests were performed on the standard device PMT-3.
2. The indent, i.e. four-sided Vickers pyramid with an angle between faces of 136 was applied.
3. The indent was moved towards the sample surface along indentation diagonal.
4. The load interval on the indent varied within range of 0.1–1.2 N.
5. The width of scratch B1 (trace of a frontal indentation diagonal), width of the fracture zone B2 of the coating or the basis and, if available, width of the separation zone B3 of the coating from the substrate were measured.

The curves of the results of the coating tests on nickel substrate by scratching technique are given in figures 4, 5.

The analysis of YSZ coating test results showed, that the scratching process at all loadings on the indent was characterized by the presence of both the fracture zone B2, and zone of the coating B3 separation as well. The presence of the developed zone B3 is very important for quantitative assessment of adhesive properties of the coatings.

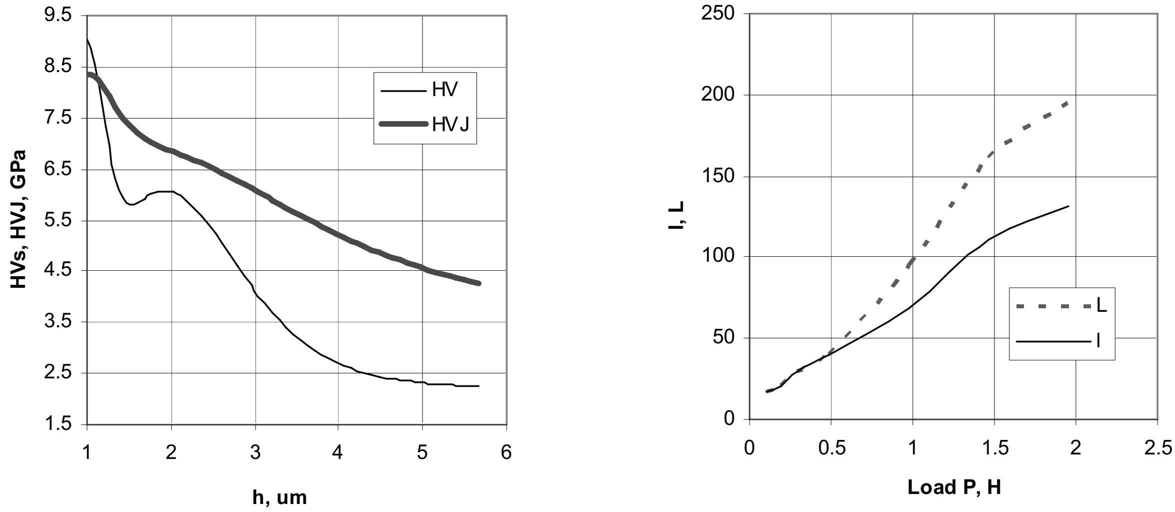
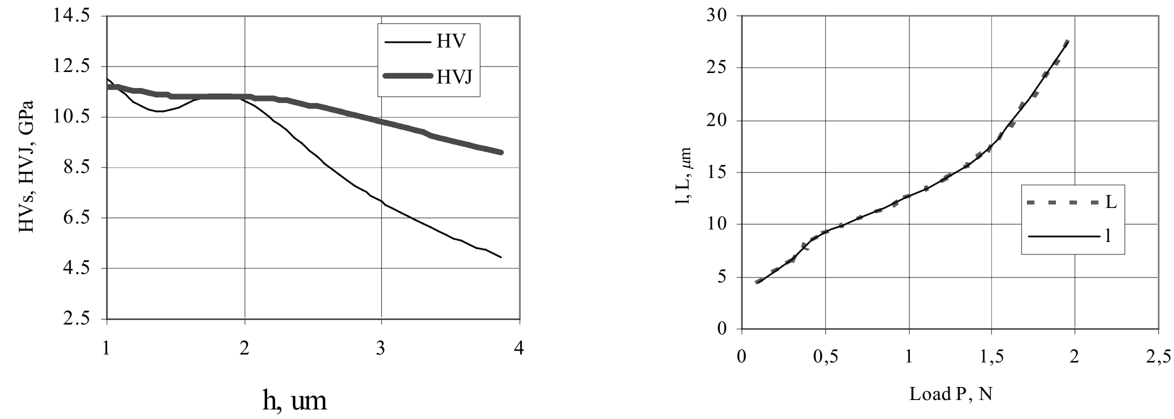


Fig. 2. Results of research of YSZ coating microhardness (10 мм) on Ni substrate (a – HV(h), HVJ(h); b – l(P), L(P))



a *b*

Fig. 3. Results of research of YSZ+Ni composite coating microhardness (15 мм) on Ni substrate (a – HV(h), HVJ(h); b– l(P), L(P))

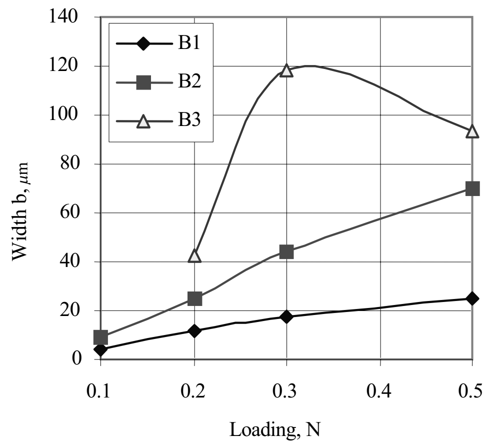


Fig. 4. Test of YSZ coating on a nickel substrate by scratching. B1 is the width of trace; B2 is the width of fracture zone; B3 is the width of separation zone

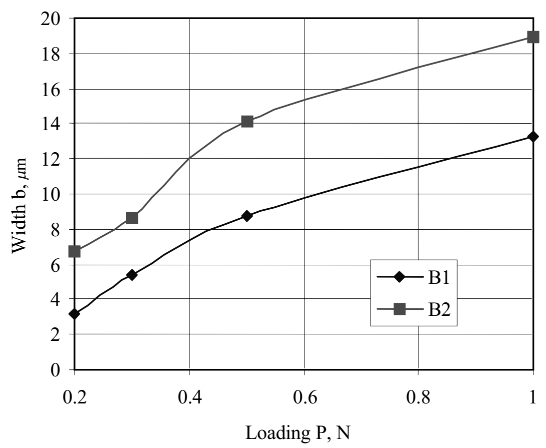


Fig. 5. Test of YSZ+Ni composite on a nickel substrate by scratching. B1 is the width of trace; B2 is the width of fracture zone

Results of tests of the nickel sample with a composite coating YSZ+Ni somewhat differ from the previous one. So, the separation zone B3 is absent for all test loadings. The width of zone B2 describing cohesive fracture of the coating, practically repeats the behavior of the width of the scratch B1 trace. The level of values B1 and B2 is approximately three times less, than for YSZ coating, and corresponds, for example, to 9 and 14 μm at scratch depth a little deeper than 1 μm at loading of 0.5 N. All this testifies to the increased cohesion and adhesive strength of the composite coating.

Results of tests by scratching can be also applied for determination of other analytical strength characteristics of the coatings, for example, energy of the coating fracture or separation. It is enough to determine differences B2–B1 or B3–B2 in the test loading interval for that. The areas under the obtained curves of differences within range of test loadings will characterize specific work of the coating fracture or its separation as the parameters of adhesive-cohesion strength.

Conclusion

The technique for calculation of HVJ integral microhardness in indentation depth function was developed on the basis of standard microhardness tests HV.

The research results showed that the developed technique for micromechanical static tests is applicable not only to a comparative evaluation of strength properties of composites coating -substrate under HV and HVJ characteristics, but also to strain and crack resistance of the coatings under the critical loading parameter of the coating P_{cr} fracture and the corresponding dimensional parameters of the indentation $l_{cr}=L_0$.

The analysis of test results of the ceramic coatings by the scratching technique testifies to a feasibility of evaluation of cohesion and adhesive properties of the YSZ-based ceramic coatings in a wide range of loadings on the indenter.

The obvious advantages of YSZ and (YSZ+Ni) based composite coatings in terms of higher strength and plastic properties, and also are fracture toughness were demonstrated by the results of the studies and integrated tests of the coatings using the developed techniques.

References

[1] *GOST 21318. Measurement of microhardness by scratching with diamond points.*

[2] V.F. Berdikov, Yu.N. Vilk, O.I. Pushkarev, E.A. Lavrenova, Strength Problems 3, 90 (1993).