MECHANICAL CHARACTERIZATION OF POST TREATED THERMAL BARRIER COATINGS USING FOUR POINT BENDING

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Abstract. Thermal barrier coatings or TBCs have been widely used, mainly on gas turbine and diesel engines. The most common material used as an insulator in such systems has been partially stabilized zirconia (PSZ) normally overlaid onto a metallic bond coat layer by plasma spraying. The obtained ceramic layer is normally porous, improving the insulating properties. However, that porosity also increases gas permeability and therefore reduces the oxidation resistance of the coating. Post-treatments have been applied in order to reduce gas permeability, mainly using sol-gel technology. In general, mechanical properties of post-treated coatings are not addressed in such studies. In this work thermal barrier coatings (TBCs) were applied on low carbon steel substrates, using two different sets of bond coat, i.e., metallic and metal-ceramic. Sol-gel was used to post-treat the coatings in order to impregnate the porous ceramic topcoat with alumina or zirconia. The samples in the as sprayed and post-treated form were characterized using four point bend tests. Acoustic emission was used to in situ monitoring cracking development under four point bending. The acoustic emission results are presented based in energy distributions, which are linked to crack behavior during the test.

Key words: Plasma Spray, Sol-gel, Coating, Ceramic, Metal

1. INTRODUCTION

Thermal Barrier Coatings (TBCs) have been extensively used in gas turbine and diesel engines (Pawlowski, 1995). Partially stabilized zirconia (PSZ) has been the most common material used as insulator in such systems, mainly due to its low thermal conductivity and diffusivity combined with its high temperature stability. The general practice in preparing thermal spray TBCs is to spray the ceramic overlay onto a metallic bond coat layer, generally

by plasma spraying. Thermal barrier coatings (TBCs) insulation and thermal resistance properties are certainly among the more important benefits reached by applying ceramic coatings (Bennet, 1986; Wigren & Pejrid, 1998). When TBCs have to face also corrosive environment, like in diesel engine applications, the natural advantages of the intrinsic porosity of the ceramic layer, that enhances insulation and strain tolerance, turn to a permeability problem. The corrosive media can reach the bond coat or even the bond coat / substrate interface causing corrosion or oxidation, in the case of hot oxygen permeation, of the metallic materials and even delamination of the coatings (Fox & Clyne, 1998; John & Troczynski, 1996). Another important factor responsible for premature failure of TBCs is that due to the residual stresses resulting from rapid solidification and differential thermal expansion between metallic and ceramic materials in the system (Pawlowski, 1995). Hence, controlling the substrate temperature during deposition has a significant influence on the nature and magnitude of residual stresses (Clyne & Gill, 1996; Kuroda, 1995). Several approaches have been investigated in order to reduce such residual stresses and improve coatings performance mainly by using functionally gradient materials (FGM) concept (Smith et al, 1996; Lima & Trevisan, 1997; Khor at al, 1998). Complementarily, intermediate cermet layers increase the permeable volume of the coatings.

The use of solution mixing followed by gelation to make glasses and ceramics of various oxide compositions was developed 40 years ago. The solution sol gel process includes three main parts: (i) mixing various oxides in solution, often using metal organic precursors; (ii) forming a sol and causing it to gel in order to retain chemical homogeneity during desiccation; and (iii) shaping during or after gelation into final shape (when making glasses or ceramics), then heat treating, leading to a xerogel (dried gel) and finally to a glass or ceramic (Roy, 1987). The sol-gel route from metal alkoxides has been more recently also used to produce oxide ceramic powders and deposits (Mehrota, 1989; Karthikeyan et al, 1997) as well as an infiltration technique to post treat porous coatings by sealing (Troczynski et al, 1998; Karthikeyan et al, 1996). The liquid sealer penetrates into the interconnected porosity by a capillary action and then solidifies.

To better understand the coating formation and failure mechanisms, the influence of spray conditions and TBC system design have been characterized by a number of distinct methods. Acoustic Emission (AE) technology has been widely used as a non-destructive method in characterizing the cracking and failure behavior of the coatings. The technique also has potential for the quality control and in-service monitoring of coatings during application or production. The method has mostly been used to understand the failure mechanisms during thermal cycling (Bordeaux, at al., 1992; Shankar, et al., 1983). Less effort has been spent in characterizing the deformation and failure behavior at room temperature conditions, under mechanical stresses. Among the few studies, experiments have monitored the *in situ* cracking of samples during three-point (Zhang et al., 1987; Berndt et al., 1983) and four-point bend tests (Lin et al., 1997; Lin, 1995; Senturk et al., 1999), tensile adhesion tests (Berndt, 1988; Shankar et al., 1983), and indentation (Safai et al., 1980) tests.

In the present work, thermal barrier coatings were applied on metallic substrates. Two kinds of bond coats were used beneath the ceramic top coat, a NiCrAl and a functionally graded material (FGM) consisted of NiCrAl and 8wt.%Yttria Partially Stabilized Zirconia (PSZ), to verify the bond coat influence on both the as sprayed and impregnated coating performance and characteristics. Sol-gel impregnation was performed in order to seal the coating porosity and reduce coating permeability. Four-point bending was applied to evaluate the mechanical response, while acoustic emission (AE) was used to *in situ* monitor the cracking behavior during these tests. The bend tests are used to provide more quantitative results with respect to the mechanical properties of the coating-substrate system. The hardness

of the coatings was measured by Vickers indentation using an BUEHLER Micromet II equipment (Buehler Ltd., Lake Bluff, IL, USA). The maximum load applied was 500 g.

2. EXPERIMENTAL PROCEDURE

2.1 Materials and Spray Conditions

Thermal barrier coatings with a metallic or a metal-ceramic bond coat were sprayed by atmospheric plasma spraying (APS) having the plasma spray gun (Metco 3MB, Metco, Westbury, NY) mounted on a six-axis articulated robot (GMF – S400, GMF Fanuc). The spray conditions are given in Table 1. Both metallic and ceramic powders were externally injected into the plasma at a rate of 40 g/min using nitrogen as the carrier gas. Two powder feeders were used to individually feed metallic and ceramic materials. Partially stabilized zirconia (ZrO_2 8wt.% Y_2O_3) was used for the top coating. The feedstock material for the bond coat was NiCrAl (metallic) and 40 % ZrO_2 8wt.% Y_2O_3–60 % NiCrAl (metal-ceramic).When applying the cermet bond coat, the two powder feeders were settled in parallel and a "T" junction was placed before reaching the powder injection region of the plasma gun. The same conditions shown in Table 1 for individual powder application were kept for cermet feeding. Prior to spraying, the surfaces to be sprayed were grit blasted and washed in ethyl alcohol. For spraying, the samples were placed on a carousel with six substrates sprayed at a time. The rotation speed of the carousel was set at 160 rpm, while the robot was programmed to provide a vertical traverse distance of 90 mm at 12 mm/s. The resulting thickness range of the coatings was 80-110 μm for the bond coat and 380-450 μm for the ceramic layer. Air jet was used to cool the substrate during spray. Spraying was performed on mild steel substrates of 60 x 20 x 2,5 mm.

Table 1. Plasma spray deposition conditions

	YSZ	NiCrAl
Gun Type	Metco 3MB	Metco 3MB
Amperage	600 A	500 A
Voltage	70 V	70 V
Primary Gas	Ar (40 l/min)	Ar (40 l/min)
Secondary Gas	H_2 (11 l/min)	H_2 (11 l/min)
Powder Carrier Gas	N_2 (3,5 l/min)	N_2 (3,65 l/min)
Spray Distance	100 mm	100 mm

After spraying, some samples were post treated by sol-gel impregnation (Brinker, 1990). The precursors for impregnation were aluminum isopropoxide dissolved in isopropyl alcohol and zirconium butoxide in n-butanol using the alkoxide route (Berezin & Troczynski, 1996). For aluminum precursor, the specimens were immersed in the solution at atmospheric pressure for 15 minutes, dried at 65 °C for 2 hours and furnace heat-treated at 600 °C for 15 minutes. In the case of zirconium precursor, the specimens were evacuated for 15 minutes to remove trapped gases inside the pores. Then, the specimens were immersed in the sol and evacuated again for 10 minutes, when the air vent was opened to the atmospheric pressure. After 10 minutes, the specimens were removed from the sol and dried at 80 °C for 1 hour. The sol filled specimens were calcined at 600 °C for one hour and heat treated at 1000 °C for one hour to obtain ceramic impregnated specimens. The furnace calcination and treatments were carried out in argon atmosphere with heating and cooling rates of 8°C/min.

The temperature of the substrate during spraying was determined using temperature indicating liquids in different measuring ranges (Omegalaq, Omega Engineering, Stamford, CT) and was confirmed using a hand held infrared temperature detector. The temperatures measured were in the 400-500°C range.

2.2 Four Point Bending Tests and Acoustic Emission

The samples were subjected to four-point bending (20 mm inner span and 40 mm outer span) using a servo-hydraulic testing machine (Model 8502, Instron, Canton, MA), with the crosshead speed set to 10 μm/sec and the load and displacement recorded for each measurement. A maximum load of 1 kN was applied to all the samples. A compliance calibration for the experimental arrangement was made using the Instron LVDT and an external LVDT (Model CD375-500, Macro Sensors, Pennsauken, NJ) that was placed close to the pin supports. This enabled a better measurement of displacement by calibrating the crosshead movement. During the tests, a piezoelectric AE transducer (pico-transducer, Physical Acoustics, Princeton, NJ) with a resonance frequency of 250 kHz was placed on the coating. The sensor was attached to a preamplifier (model 140B, Hartford Steam Boiler Inspection Technologies, Sacramento, CA) and a preamplifier filter (model FL12Y, Hartford Steam Boiler Inspection Technologies, Sacramento, CA), with an amplification of 40 dB and the frequency range analyzed at 10 kHz-1 MHz. The signal output was processed using an AET 5500 system (Hartford Steam Boiler Inspection Technologies, Hartford, CT), which was connected to a redundant PC to record the acoustic emission (AE) responses. Procedures with regards to the experimental setup and AE signal processing are available elsewhere (Lin, 1995). A total of five samples were tested for each condition. Prior to testing, the sample surfaces were polished to a 1 μm diamond finish and the specimens were stored in a desiccator. The microhardness of the coatings was measured on the polished surfaces.

3. RESULTS AND DISCUSSION

Microhardness measurement results are shown in Table 2. No significant difference in the measured values can be identified. Heat treated samples without impregnation are incorporated in Table 2 for both types of bond coat series in order to observe the influence of heat treatment itself, which is applied to the sol-gel impregnated samples. The heat-treated samples (MHT, with a metallic bond coat and heat-treated and MCHT, with a metal-ceramic bond coat and heat-treated) were submitted to the same temperatures of zirconia impregnated samples as described before.

Table 2. Microhardness results for the coatings (HV $_{500g}$)

Coating System	Measurements									
	1	2	3	4	5	6	7	8	9	10
M	431	448	466	460	378	386	411	413	420	386
MC	386	338	380	440	423	475	298	342	442	497
MHT	399	272	362	356	351	339	492	325	353	473
MCHT	247	383	414	311	292	497	402	362	477	416
MA	458	385	318	475	418	396	380	373	399	466
MCA	413	516	470	414	420	368	516	458	339	475
MZ	448	402	393	436	479	511	577	365	552	523
MCZ	371	552	528	563	399	479	368	557	468	580

Figure 1 shows the results from Table 2 in a graphical way by using average and standard deviation values.

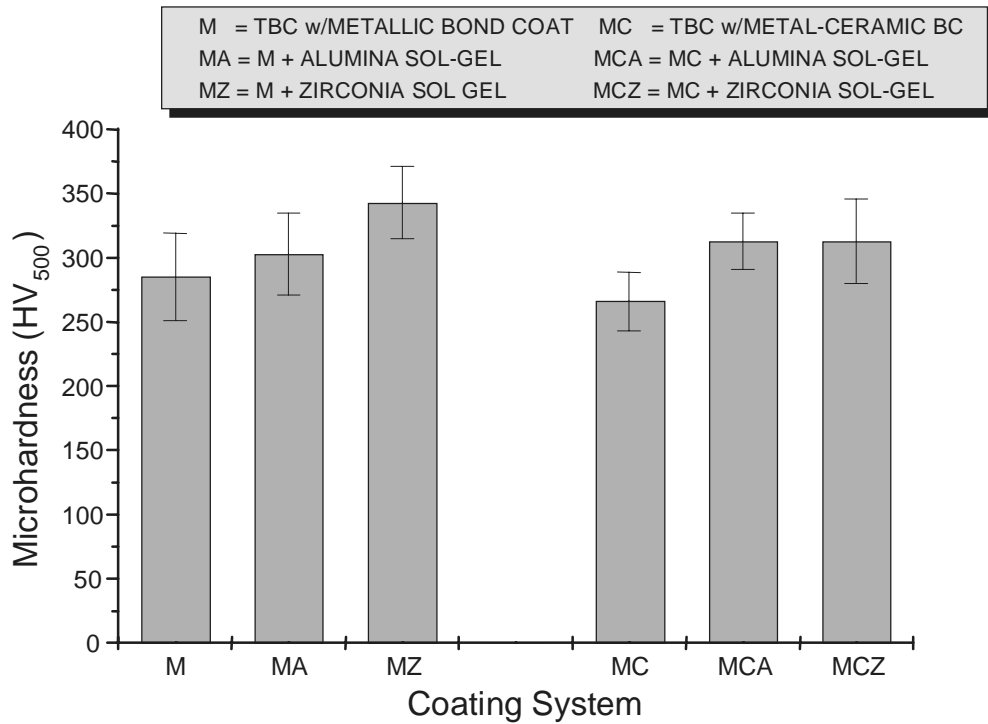| M = TBC w/METALLIC BOND COAT | MC = TBC w/METAL-CERAMIC BC |
| MA = M + ALUMINA SOL-GEL | MCA = MC + ALUMINA SOL-GEL |
| MZ = M + ZIRCONIA SOL GEL | MCZ = MC + ZIRCONIA SOL-GEL |

Figure 1. Microhardness comparison among the coating systems

As can be observed from Fig.1, microhardness decreases 6,6 % in average for the TBC coatings with a metal-ceramic bond coat in the as sprayed condition if compared to values observed for the coatings with a metallic bond coat. For the sol-gel alumina and zirconia impregnated samples, in the metallic bond coat group (MA and MZ), microhardness increased 6,3 % e 20,3 %, respectively. In the metal-ceramic bond coat group, the sol-gel impregnated samples presented an average increase of 17,65 % for both alumina and zirconia series (MCA and MCZ, respectively) compared to the as sprayed TBC with a metal ceramic bond coat (MC).

The results from four-point bending tests are presented as load-displacement curves in Figures 2 and 3 for the groups of coatings with a metal-ceramic or a metallic bond coat, respectively. Five samples of each condition have been tested. The general behavior for each coating system is recognized to remain almost constant during the tests.

The load displacement curves for the different coating systems can be represented in a same graphic figure to improve visual comparison (Fig. 4). The plotted curves are representatives from each individual group of Fig. 2 and Fig 3.

All the curves in Figure 4 show an initial linear range, which then changed to a non-linear portion, indicative of an elastic-plastic response. The initial non-linear "toe" region can also be recognized, and is attributed to the arrangement of the loading and support bars on the sample. This behavior of the composite system arises since the composite consists originally of a steel substrate and a metallic or metal ceramic bond coat under a ceramic topcoat. Hence, the transition from the elastic to plastic regions can be related to the behavior of the metal substrate, with the deformation characteristics of the metal substrate dominating after yielding.
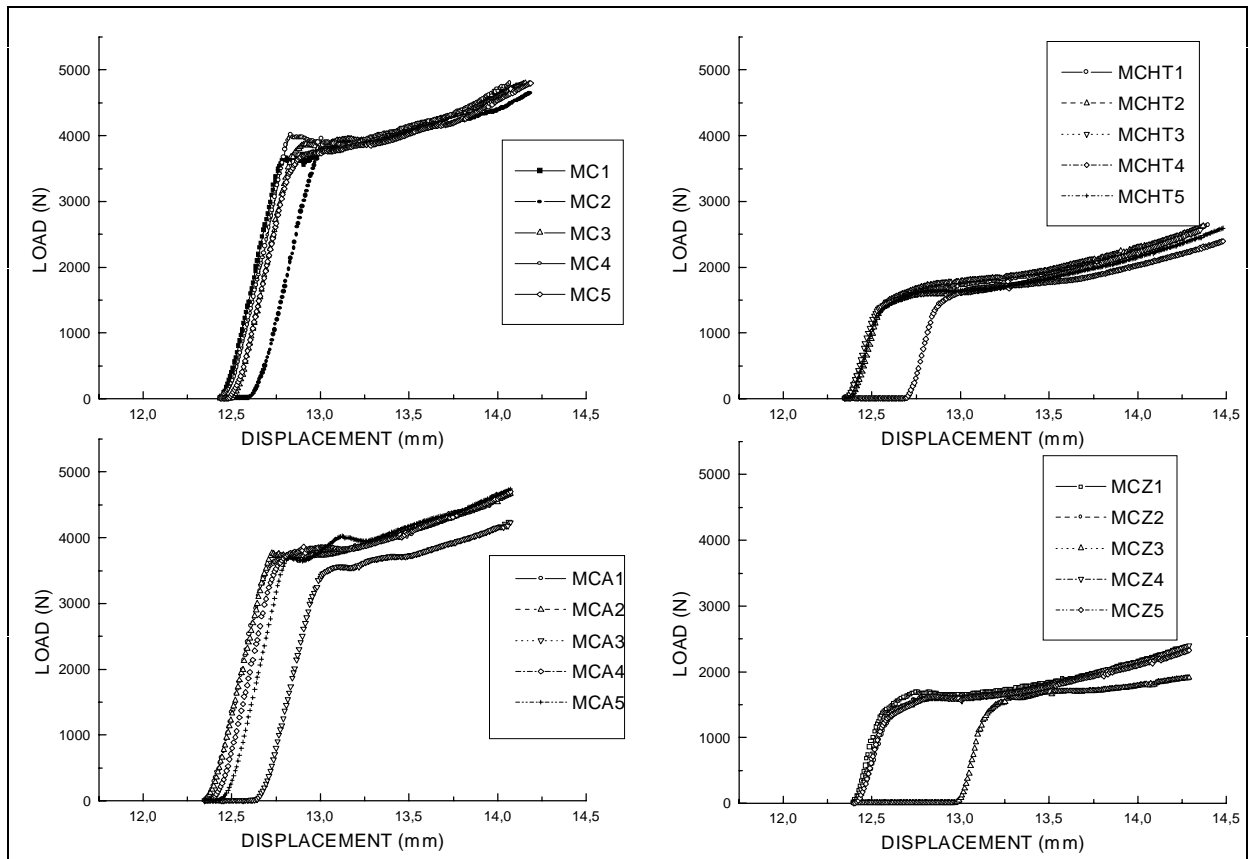
Figure 2. Load – displacement curves for the coatings with a metal-ceramic bond coat
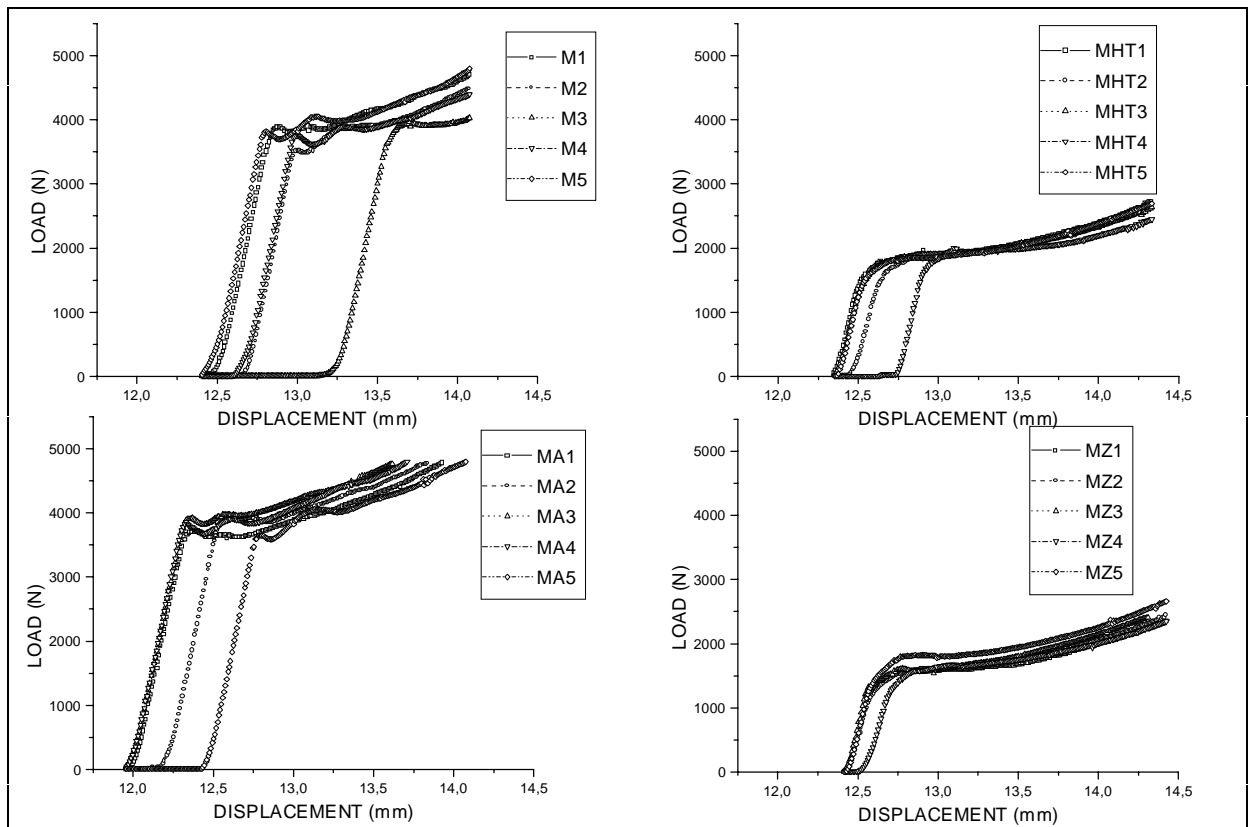

Figure 3. Load – displacement curves for the coatings with a metalllic bond coat
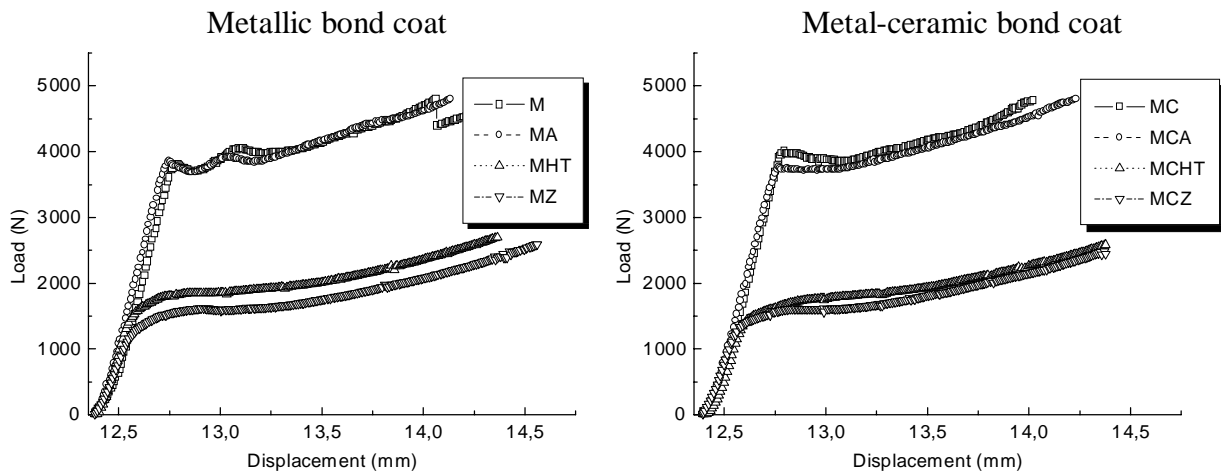
Figure 4. Comparative load-displacement curves for coatings with different bond coats

The ceramic coating, together with the bond coat layer, on the steel substrate has a significant influence on the load-displacement curve prior to yield. This fact can be recognized by the presence of a peak transition region between the elastic and plastic portions, suggesting that the coating is structurally contributing to the material responses of the composite structure until yielding. Therefore, this behavior indicates that the coating is inhibiting yield of the composite system with respect to the usual behavior of the metal substrate where there is a smooth transition region. Thus, the coating appears to strengthen the system and the yield point is elevated. Accordingly, the peak load can be related to the failure of the coating (Senturk et al., 1999). For samples heat-treated at 1000 °C for 1 hour (MHT, MZ, MCHT and MCZ), the behavior of the substrate-coating system is changed and then the load-displacement curves show a smooth elastic –plastic transition region, like the metal substrate curves whit no coating. This could be related to the metallurgical effects of the heat treatment at high temperature on the substrate material.

The changes in the yield stress for samples of the eight distinctive coating systems are shown in Figure 5. A significant feature can be recognized from Fig. 5 where a smaller value
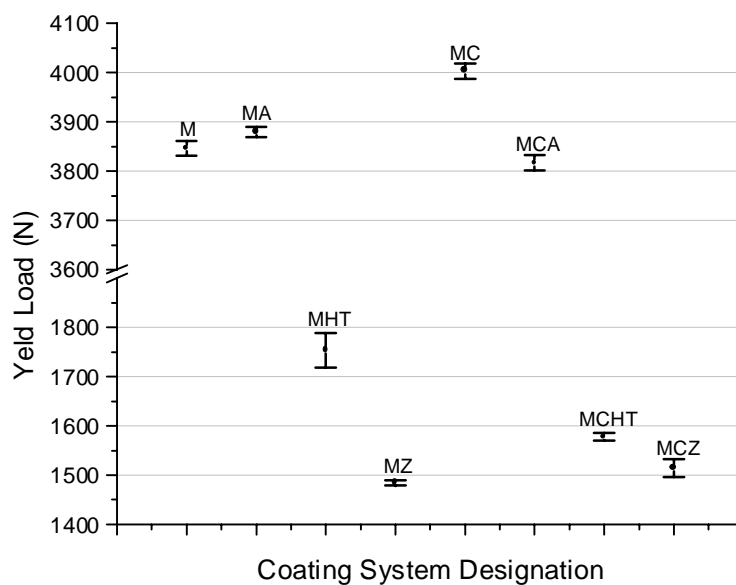

Figure 5.Yeld Load for the different coating systems

of the average yield load is present for samples that were submitted to a higher temperature in the heat treatment (1000 °C for the samples impregnated with zirconia and then heat treated, MZ and MCZ, and samples only heat treated, MHT and MCHT), while the other samples heat treated at 600 °C (MA and MCA) or without heat treatment (M and MC) have much higher results. This indicates that *(i)* the heat treatment has a critical influence on the results, even reducing the conventional yield load for the tested steel substrate, that is around 2600 N (Senturk et al, 1999b), by annealing and *(ii)* the sol-gel impregnation itself either with alumina or zirconia has a minor effect on the yield load, which is dominated by substrate properties and the influence of the coating. The presence of a coating increases the yield load. This behavior can be explained on the basis of the role of the bond coat layer, where, among its other features, it is also known (Bennet, 1986) to act as a compliant layer in decreasing the thermal expansion mismatch between the ceramic coating and the metal substrate. The benefit from this behavior, which is normally intended to be dominant at high temperatures, is that the ceramic overlay is isolated from high strain and hence, is prevented from spallation (Bennet, 1986). For repeated thermal cycling, this continues until the bond coat can not plastically deform; i.e., creep.

The acoustic emission data are plotted in Figure 6 in terms of energy for each individual coating system.
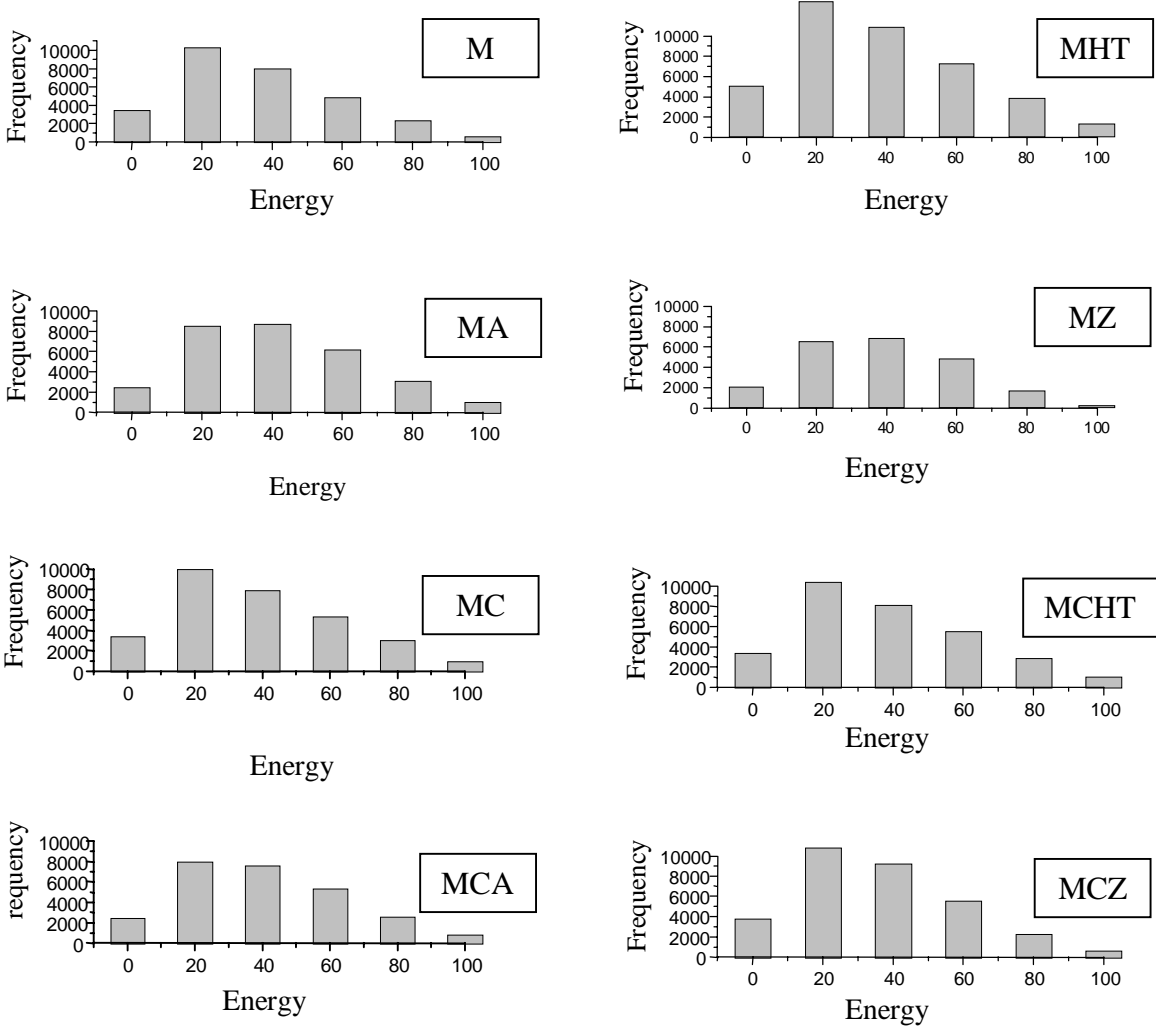

Figure 6. Frequency histogram for acoustic emission energies registered
during four point bending tests

According Lin (1995), the energies in the range of 0 to 40 can be related to microcrack events, in the range of 40 to 80 they can be related to transition crack events and above 80 they can be related to macrocrack events. From Fig. 6 observation, a slightly higher incidence of microcracks can be observed for the group of samples that were submitted to high temperature heat treatment (MHT, MCHT and MCZ). Only the MZ system did not showed this behavior, having a lower frequency for all energy levels. Fracture surface analysis will be helpfull to clarify this point.

4. CONCLUSIONS

The mechanical properties and deformation characteristics of PSZ coatings are shown to be significantly influenced by heat treatment of the samples at temperatures around 1000 °C as it occurs for sol-gel zirconia impregnated samples in order to obtain a denser ceramic coating. A strong reduction in the yield load was observed for that coating systems, not depending on the type of bond coat used. The presence of a metallic or a metal-ceramic bond coat layer did not show strong influence in the mechanical behavior of the coatings in four-point bending tests. The post-treatment with sol-gel impregnation has showed to significantly increase microhardness of samples, regardless to the type of bond coat applied.

The AE analysis during bending tests shows that the cracking phenomena in these samples change. The overall analysis of the results indicate that heat treatment of impregnated samples should be done in a "local" basis, trying to evitate the simultaneous heat treament of the substrate, which drastically reduce its yield point leading to a premature failure of the substrate-composite system.

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