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Prepared for
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INTRODUCTION

Currently, there is considerable interest in the use of insulating ceramic thermal barrier coatings (TBCs) on cooled hot section components of gas turbines. These coatings are presently being developed for both clean-fuel aircraft gas turbines and the anticipated dirty-fuel environments of industrial/utility gas turbines. Such insulative coatings can give temperature drops of 100° to 200° C when only 0.04 cm thick. This large temperature drop offers substantial potential gains in heat engine efficiency by permitting higher gas temperatures with no change in component temperature or in durability by lowering metal temperature. The basis for the current interest in ceramic TBCs was brought about by the good performance of such coatings in clean fuel combustion gas exposures (refs. 1 to 3). However, early results with the ZrO_2-$12Y_2O_3$/NiCrAlY system in the presence of the usual heavy fuel impurities (Na, V, etc.) were less than encouraging (ref. 4). In burner rig tests at NASA Lewis, two coatings systems, ZrO_2-$8Y_2O_3$ and a calcium silicate TBC, were identified as having substantially more resistance to spalling in Na plus V doped combustion gases than previously tested systems (ref. 5). A number of TBCs based on calcium silicate, on improved ZrO_2-Y_2O_3 compositions, and on improved NiCrAlY and CoCrAlY bond coats were evaluated recently in similar burner rig hot corrosion tests. The purpose of this paper is to present and discuss these results.

EXPERIMENTAL PROCEDURE

Materials and plasma spray coating deposition. - The chemical compositions and specifications for 1.8 CaO SiO_2 and ZrO_2-Y_2O_3 plasma spray powders and cast nickel-base alloy IN-792 hollow erosion bar substrates have been documented previously (refs. 3 and 5). All plasma spray bond coats were analyzed and found to have trace impurity levels comparable to the levels in bond coats used in reference 3. Both thermal barrier and bond coatings were applied manually in an open-air environment with a subsonic plasma spray gun using argon as the plasma gas. Metallographically measured coating thicknesses varied locally from 0.005 to 0.018 cm for a nominal 0.013 cm thick coating, and by about ±0.010 cm for all thicker coatings. The zirconia coatings were about 88 percent dense with interconnected porosity while calcium silicate coatings were more dense and had fewer interconnected pores.

Cyclic Mach 0.3 burner rig tests. - The Mach 0.3 burner rig used in these studies is described in reference 5. Briefly, air, fuel, and an aqueous solution of NaOH and NH_4VO_3 were injected into the combustor, ignited, and expanded through a nozzle at a velocity of Mach 0.3. The dopant levels of Na and V in the combustion gases were adjusted to correspond to a fuel equivalent of 5 ppm Na and 2 ppm V. Cooling air flow was calibrated to maintain the metal substrate at 843° C for 0.038 cm ZrO_2-$8Y_2O_3$ coated specimens. Test parameters based on the calibration runs were: fuel/air mass ratio of 0.046, calculated adiabatic flame temperature of 1552° C, coating surface temperature of 982° C, metal substrate temperature of 843° C, specimen holder rotation of 450 rpm, and specimen distance from the nozzle of 3.2 cm.

Coated specimens were exposed to thermal cycles consisting of 1 hour at temperature followed by 6 minutes of external forced air cooling to below 100° C. Internal cooling air was maintained constant during both heating and cooling cycles. Specimens were inspected after each twenty 1-hour cycles. Specimens were removed when the ceramic had spalled over approximately one-fourth of the hot zone on the leading edge. Coating lives reported represented the average removal time of two specimens, but individual variations in life generally were no more than ± 15 percent from that average. A representative number of exposed specimens were selected for metallographic (all specimens polished in varasol to retain water soluble condensates), XRD, SEM, EMP, and chemical analyses to determine the extent of hot corrosion and to identify condensates and the mode of spalling.

RESULTS AND DISCUSSION

Test results. - The response of the TBCs to the Na plus V doped Mach 0.3 combustion gases is summarized in figure 1. In general the data show (1) that the durability of TBC systems may be substantially improved by reducing the thickness of the TBC from 0.038 to 0.013 cm, (2) that high Cr+Al bond coatings improve the durability of TBC systems, (3) that 1.8 CaO SiO_2 coatings are more durable than ZrO_2-$8Y_2O_3$ at comparable ceramic thicknesses with the same bond coatings, and (4) that ZrO_2-$12Y_2O_3$ and ZrO_2-$6Y_2O_3$ TBCs are less durable than ZrO_2-$8Y_2O_3$ TBCs when evaluated with the same baseline bond coating. Specimens with 0.013 cm thick ceramic coatings have higher bond coat and lower ceramic surface temperatures compared to specimens with 0.038 cm thick ceramic coatings. If the temperatures within the ceramic coating or at the bond coat/ceramic interface are higher than the dew points of the condensates (e.g., 905° C for Na_2SO_4) no condensation can occur at this location which may account for the increased durability of TBC systems with thinner ceramic coatings. No apparent hot corrosion of the bond coatings was evident from metallographic examination of the tested specimens. The improved durability of TBC systems with various bond coatings thus may not be due to differences in bond coat hot corrosion resistance.

Analyses of test specimens. - Two modes of spalling of the TBCs were observed for specimens exposed in these hot corrosion tests. 1.8 CaO SiO_2 coated specimens spalled in the center of the hot zone. In a few cases, as with YSZ coated specimens, they failed at the upper edge of the hot zone as illustrated in figure 2. Points A, B, and C in figure 2 show where cross-sections were taken for metallographic and EMP analyses and points D, E, and F show where samples were taken for SEM/EDAX, chemical, and XRD analyses.

The post-test analyses of some representative specimens are summarized in table I. X-ray data for 6 and 8 w/o YSZ indicated no gross changes in the tetragonal to monoclinic ratio. XRD of exposed calcium silicate coated specimens showed the following: (1) There was a phase change of ß-Ca_2SiO_4 (larnite) to $CaSiO_3$ (wollastonite). Further testing is needed to determine if this phase change was reaction or thermally induced. (2) $CaSO_4$ was formed in both hot and relatively cold areas of 1.8 CaO SiO_2 test specimens, probably by a gas-phase reaction with SO_2. Calcium sulfate has also been observed in similar tests at Westinghouse (R. J. Bratton, private communication) and calcium silicate/SO_2 reactions have been reported in reference 6. SEM/EDAX and chemical analyses show that Na, S, and V are present at the surface or within exposed YSZ and 1.8 CaO SiO_2 coatings. These are probably the reaction and condensation products of Na_2SO_4, $Na_2V_2O_6$, and V_2O_5. Co, Fe, W, and Ni, found only in 1.8 CaO SiO_2 coatings, probably evolved from the L-605 Co-based Mach 0.3 burner rig nozzle.

The results of EMP mapping studies of exposed ZrO_2-$8Y_2O_3$ and calcium silicate coated specimens were in general agreement with the XRD, chemical and SEM/EDAX analyses. In figure 3(a) there is good correspondence between Na and S in a ZrO_2-$8Y_2O_3$ coated specimen and this is taken as evidence that Na_2SO_4 formed in the flame and condensed in coating pores and cracks. The scans of V (not shown) and Y indicated local concentrations of Y and some correspondence with V in some of these areas (probably YVO_4). Additional EMP scans on the same specimen at the colder A and C sections show some correspondence between Na, S, and Y and between S and Y which is believed to be the possible formation of $Y_2(SO_4)_3$ or Y_2S_3. EMP scans of Ca, Si, S, Na, V, Co, and W in a typical calcium silicate specimen at the A section show several interesting features (fig. 3(b)). This specimen had spalled in the hot zone as indicated in figure 2. There is almost a 1:1 correspondence of Na and S indicating Na_2SO_4 formation and some V and Na overlap at the surface which is probably $Na_2V_2O_6$. Of the elements evolving from the L-605 nozzle, only Co penetrated calcium silicate to any extent. Additional S in the interior of the coating is taken as an indication of $CaSO_4$ formation below the surface. EMP scans of the B section of the same specimen in the hotter spalled area show S ($CaSO_4$ from SO_2 reaction with 1.8 CaO SiO_2) and very little if any Na within the entire 0.005 to 0.013 cm remaining coating. However, the bulk of the coating was still calcium silicate based on the EMP scans of Si, Ca, and XRD results.

Calculation of dew points of potential condensates. - Based on calculations similar to those in reference 7 and the temperatures shown in figure 1, either V_2O_5 (l) (dew point 1210° C) or $Na_2V_2O_6$ (l) (dew point 1155° C) should condense and penetrate the zirconia coatings over the entire specimen length. Na_2SO_4 (l) (dew point, 905° C) should only condense outside the hot zone and penetrate only to a limited extent. Spallation of YSZ coated specimens occurred at the edge of the hot zone which implies that Na_2SO_4 (l) played a key role in causing failure of these coatings. Coating spallation may be caused by solidification of salt in the pores and microcracks of the coating which results in compressive stresses because the microcracks cannot fully close upon further cooling. EMP analyses show Na_2SO_4 within the ZrO_2-$8Y_2O_3$ coating which tends to support this argument. On the other hand EMP data also showed that reactions occurred between some Y-rich areas and S- and V-containing condensates. This could destabilize ZrO_2-Y_2O_3 and cause in spallation due to the thermal expansion difference between tetragonal and additional monoclinic zirconia.

The spalling behavior of calcium silicate is complicated. Most calcium silicate coated specimens spalled in the hot zone. Failure in the hot zone is believed to be due to a gas-phase temperature-dependent reaction of SO_2 with calcium silicate to form $CaSO_4$. Based on EMP data, spallation of a few calcium silicate coatings at the edge of the hot zone appears to be due to penetration of Na_2SO_4, $Na_2V_2O_6$, and Co containing condensates. Further exposure studies followed by analyses will be needed to clarify the mechanism of calcium silicate coating spallation and determine how the phase change of β-Ca_2SiO_4 (larnite) to $CaSiO_3$ (wollastonite) affects this mechanism.

SUMMARY OF RESULTS

The lives of 1.8 CaO SiO_2 and ZrO_2-$8Y_2O_3$ thermal barrier coatings exposed to Mach 0.3 Na plus V doped combustion gases were about four times longer when the ceramic thickness was reduced from 0.038 to 0.013 cm. High Cr + Al, Ni-31Cr-11, Al-.5Y and Ni-16Cr-13Al-.4Y bond coatings improved the durability of calcium silicate and ZrO_2-$8Y_2O_3$ TBCs by approximately 2X to 3X. Similarly, Co-22Cr-13Al-0.3Y and Co-20Cr-9Al-.4Y bond coatings improved the durability of calcium silicate TBCs approximately 3X and 2X, respectively. Chemical and electron microprobe analyses supported the predictions of condensate compositions and their role in inducing spalling of ZrO_2-$8Y_2O_3$. Calcium silicate coating failure involved condensation and penetration of Na, V, and Co containing condensates, $CaSO_4$ formation as a result of reaction with SO_2, and the phase change from β-Ca_2SiO_4 (larnite) to $CaSiO_3$ (wollastonite).

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TABLE I. - PRE- AND POST-TEST ANALYSES

Coating system* test time	Location of analyses**	XRDA		Chemical analyses		Impurities detected by SEM/EDAX
		Pre-test	Post-test	Atomic absorption	X-ray fluorescence	
ZrO_2-$8Y_2O_3$/	D	Tetragonal(s), Monoclinic(w)	Same	Na[b]	S	V,Ni
Ni-16Cr-6Al-.31Y	E	" "	"	Na[b]	S	V
120 1-hour cycles						
ZrO_2-$6Y_2O_3$/	D	Tegragonal(s), Monoclinic(w)	Same	Na[b]	S	V[c]
Ni-16Cr-6Al-.31Y	E	" "	"	Na[b]		V[c]
80 1-hour cycles						
1.8CaO·SiO_2/	D	βCa_2SiO_4(s) Larnite	$CaSiO_3$ Wollastonite(s), CeO_2(w)	Na	S	Na,S,Co,W,Ni,Ce
Co-22Cr-13Al-.3Y	E	" "	$CaSiO_3$, CeO_2(w), $CaWO_4$(w)	Na[b]	S	V,S,Co,Ni,W,Ce
620 1-hour cycles	F	" "	$CaSO_4$(s), $CaWO_4$(s), $CaSiO_3$(w)	Na[b]	S	V,S,Co,Ni,Fe,Ce
	FF[a]					S,Ce
1.8CaO·SiO_2/	D	βCa_2SiO_4(s) Larnite	$CaSiO_3$(s), NiO-CoO(s)	Na	S	Na,S,V,Co,Fe,Ni,Ce
Ni-16Cr-6Al-.31Y	E	" "	$CaSO_4$(w), $CaSiO_3$(m), CeO_2(s)	Na	S	S,V,Fe,Ni,Ce
160 1-hour cycles	F	" "	$CaSO_4$(s), CeO_2(s), $CaSiO_3$(w)	Na[b]	S	S,V,Co,Fe,Ni,Ce
	DD[a]					S,Ce

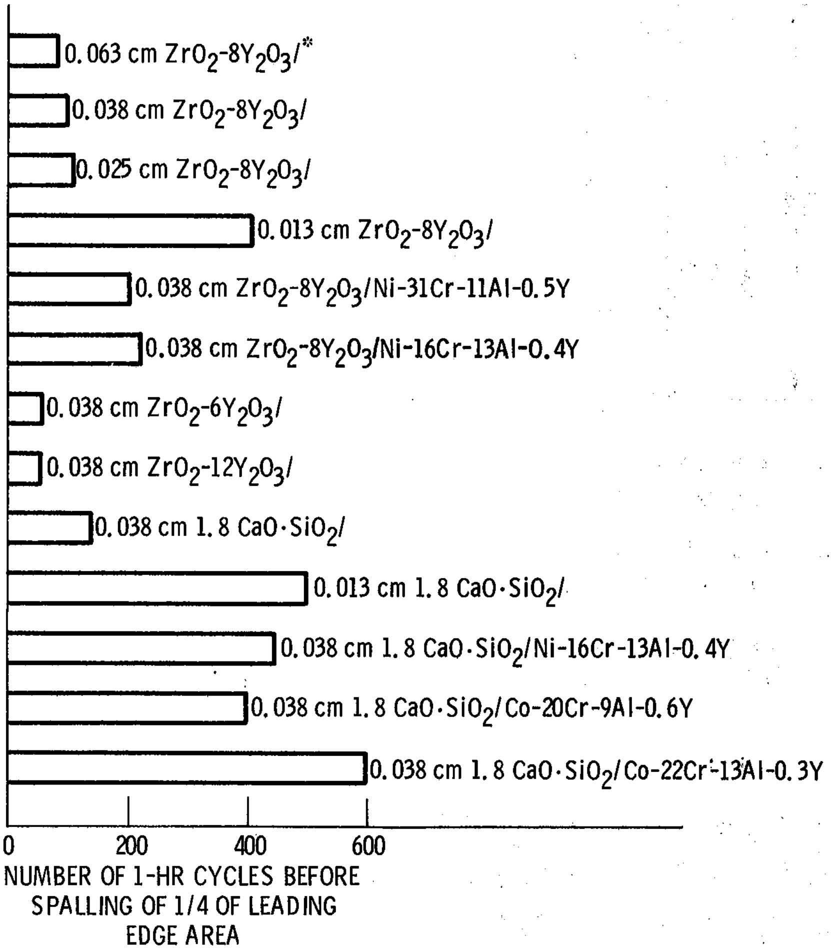
*0.038 cm thick ceramic coatings for coating systems listed.

**Calcium silicate coated specimens with failure patterns of left-hand specimen in figure 2.

[a] Sample taken at approximate depth of 0.020 cm compared to all other samples taken 0 to 0.013 cm from surface.

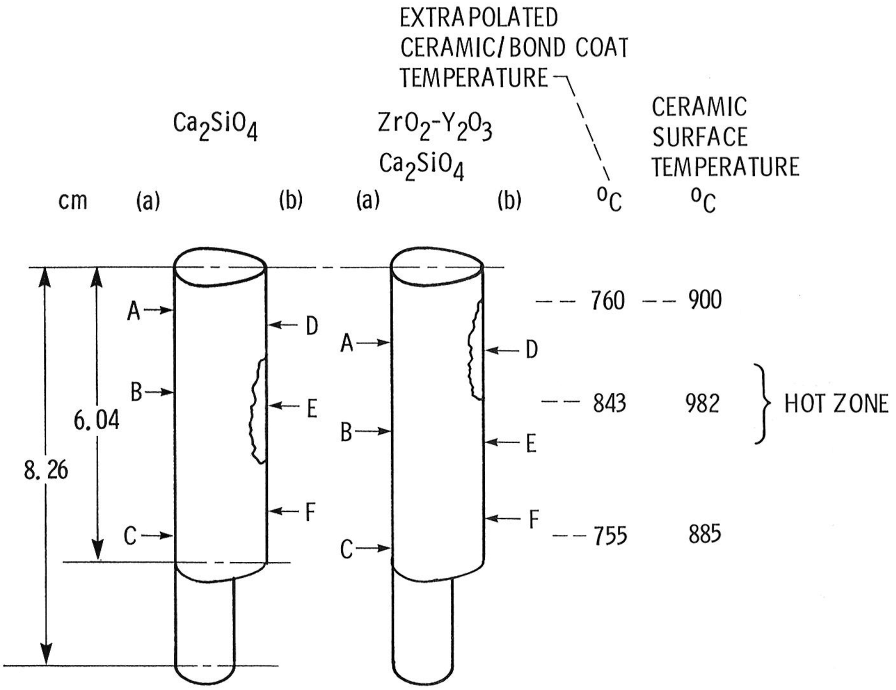
[b] Approximately twice the background amount of Na. S was present in these samples.

[c] Just discernible above background.



*BOND COATING IS 0.013 cm Ni-16Cr-6Al-0.3Y UNLESS OTHERWISE SPECIFIED.

Figure 1. - Mach 0.3 burner rig corrosion test: fuel impurity level, 5 ppm Na + 2 ppm V; fuel/air = 0.046; ceramic surface temperature, 982° C; substrate temperature, 843°C.



a A, B, AND C DENOTE LOCATIONS OF CROSS-SECTIONS FOR METALLOGRAPHY AND ELECTRON MICROPROBE SPECIMENS

b D, E, AND F DENOTE LOCATIONS WHERE SAMPLES WERE TAKEN FOR XRD, CHEMICAL AND SEM/EDAX ANALYSES

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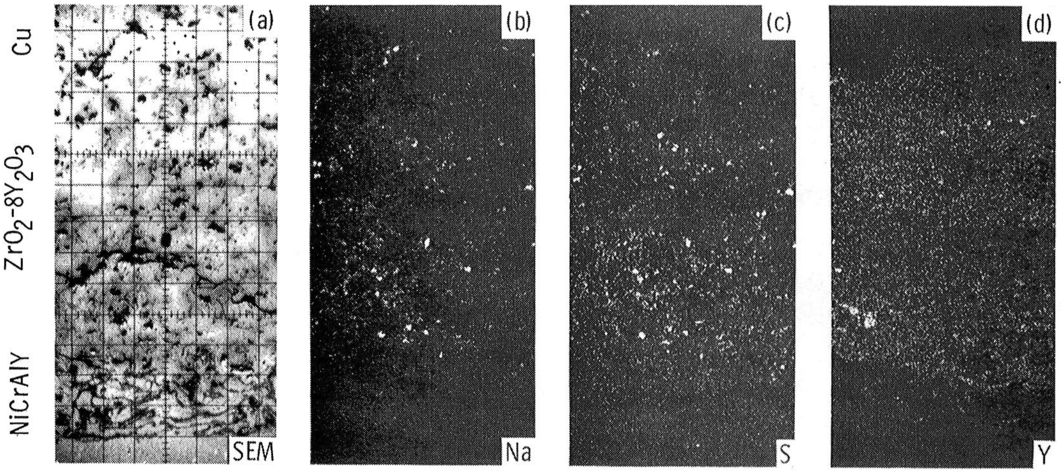
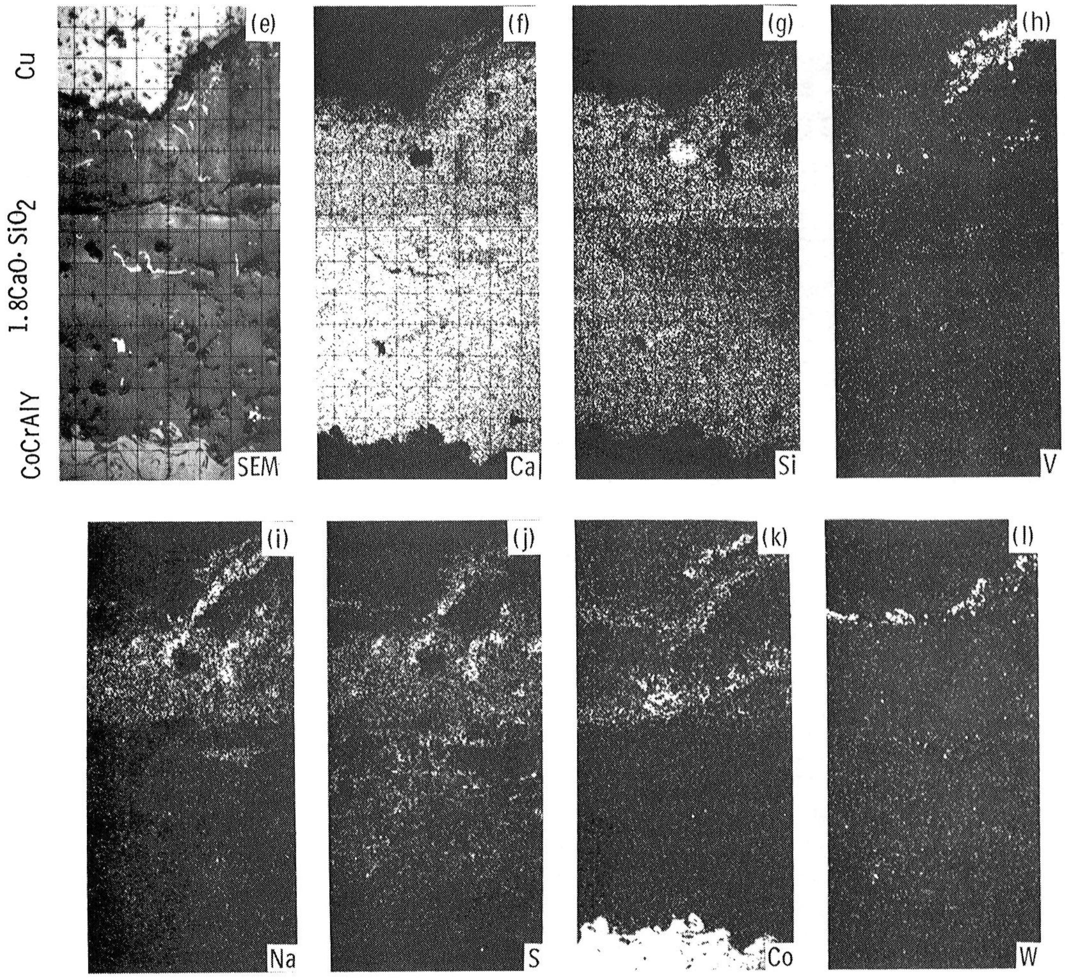
Figure 2. - Typical failure pattern of thermal barrier coatings after exposure to Mach 0.3 Na plus V doped combustion gases.



(a) ZrO_2-$8Y_2O_3$/Ni-16Cr-6Al-0.31Y COATING SYSTEM AFTER 120 1-hour CYCLES, CROSS-SECTION B, LEADING EDGE.

Figure 3. - Electron microprobe maps.



(b) 1.8CaO· SiO$_2$/Co-22Cr-13Al-0.3Y COATING SYSTEM AFTER 620 1-hour CYCLES, CROSS-SECTION A, LEADING EDGE.

Figure 3. - Concluded.

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16. Abstract

Calcium silicate and yttria stabilized zirconia/MCrAlY thermal barrier coating systems on air-cooled specimens were exposed to sodium plus vanadium doped Mach 0.3 combustion gases. Thermal barrier coating endurance was determined to be a strong inverse function of ceramic coating thickness. Coating system durability was increased through the use of higher Cr + Al NiCrAl and CoCrAlY bond coatings. Chemical and electron microprobe analyses supported the predictions of condensate compositions and the determination of their roles in causing spalling of the ceramic coatings.

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