



Effect of oxygen/fuel ratio on the in-flight particle parameters and properties of HVOF WC-CoCr coatings

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ARTICLE INFO

Available online 3 April 2011

Keywords:

HVOF thermal spray
In-flight particle parameters
WC-CoCr
Coatings
Hardness
Wear

ABSTRACT

High Velocity Oxy-Fuel (HVOF) spray techniques can produce high performance alloy and cermet coatings for applications that require wear resistant surfaces. In HVOF process, the particle velocity and temperature determine the resultant coating properties and in many cases enables a better understanding of the process. The aim of this study is to investigate influences of different oxygen/fuel ratios on velocity and temperature of flying particles as well as properties of the HVOF thermal sprayed WC-CoCr coatings. Particle parameters were recorded just prior to impact on the substrate using in-flight particle diagnostic tool Accuraspray-g3®. Detailed correlation of particle parameters and the coating properties are evaluated in order to deduce particle parameter ranges providing coatings with optimum properties.

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1. Introduction

High Velocity Oxy-Fuel (HVOF) spray technique is a thermal spray process characterized by a flame velocity up to 2000 m/s, which results in the formation of spray particle stream with relatively high velocity of the particles ($400 \text{ m} \cdot \text{s}^{-1}$ – $800 \text{ m} \cdot \text{s}^{-1}$). The temperature experienced by the particles in this process is, typically, in the range 1600°C – 2200°C , somewhat lower than that for certain other thermal spray approaches, such as plasma spraying [1–3]. Accordingly, HVOF spray process produces coatings with low porosity, and consequently high density and hardness.

The coating properties are influenced not only by the properties of the used powders but also significantly by the used spray process and spray parameters. For this reason, the production of HVOF coatings requires the careful control of the process variables together with the design and geometry of the spray gun.

In recent years, the development in process diagnostics enables on-line particle monitoring [4,5]. One of these systems is the Accuraspray-g3 system that allows the on-line measurement of temperature and velocity of sprayed particles. Particle velocities are obtained from cross-correlation of signals which are recorded at two closely spaced locations. The temperatures again are determined by two-color pyrometry.

The aim of this study is to investigate the influence of different type of fuel (kerosene and hydrogen) and the ratio of oxygen/fuel on the velocity and temperature of flying particles as well as on the microstructure and properties of high velocity oxygen fuel sprayed WC-CoCr coatings.

2. Experimental

2.1. Coating materials and spraying systems

A conventional, spherical, agglomerated and sintered WC-10 wt.% Co-4 wt.% Cr powder obtained from Sulzer Metco WOKA GmbH (Woka-3655) was employed as the feedstock powder. The agglomerate powder was received with a nominal size distribution within the range of $10 \mu\text{m}$ to $38 \mu\text{m}$ and was sprayed in this form.

A HVOF Sulzer Metco thermal spray facility was used for thermal spraying of the WC-CoCr powders. Coatings were HVOF-sprayed from the feedstock powder using two different gun-fuel combinations. The first system, which will be referred to as the Wokajet-400, was operated using kerosene as liquid fuel, and the second system, DJ-2600 (Diamond Jet 2600), was operated using hydrogen as gas fuel.

All coatings were deposited onto rectangular AISI 4340 steel specimens, which were grit-blasted before spraying. All specimens were mounted on the circumference of a horizontally rotating turntable and cooled during and after spraying with compressed air jets. The guns were attached to an ABB IRB 2400/16 robot controlling the vertical movement. In all cases the orientation of the spray gun was perpendicular to the substrates.

The various set of parameters used to spray the feedstock powder are shown in Table 1. These parameters were selected in order to obtain diverse gas flow rates and different stoichiometric combustion ratios in order to evaluate their influence in the coating properties.

The Accuraspray-g3 system was used to determine the effects of variations in the fuel characteristics and the total gas flow on the particle velocity and temperature range. The sensor head was positioned at 200 mm from the plume centre line with a standoff distance of 300 mm and 260 mm from the nozzle exit, which was the

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Table 1

Spraying parameters, in-flight particle characteristics and properties of WC-CoCr coatings (mean values/standard deviation).

HVOF gun	Test	Kerosene flow rate l·h ⁻¹	Oxygen flow rate [l·min ⁻¹]	Stoich. comb. ratio	Particle velocity m·s ⁻¹	Particle temperature °C	Roughness Ra [μm]	Porosity [%]	Microhard. HV0.3	Specific wear rate [m ³ ·(m·N) ⁻¹ × 10 ⁻¹⁸]
Wokajet-400	W1	23.1	709	0.90	730 ± 3.6	1828 ± 4.1	–	–	–	–
	W2	23.1	749	0.96	741 ± 2.0	1836 ± 2.1	–	–	–	–
	W3	23.1	769	0.98	747 ± 1.9	1838 ± 1.8	–	–	–	–
	W4	23.1	788	1.01	750 ± 3.0	1838 ± 2.9	–	–	–	–
	W5	23.1	820	1.05	761 ± 1.8	1840 ± 1.5	3.25 ± 0.14	0.45 ± 0.08	1220 ± 93	8.7 ± 1.9
	W6	23.1	850	1.08	770 ± 1.6	1842 ± 2.2	3.00 ± 0.10	0.57 ± 0.08	1220 ± 91	7.5 ± 1.7
	W7	23.1	875	1.12	773 ± 1.3	1838 ± 1.7	–	–	–	–
	W8	23.1	900	1.15	779 ± 1.0	1835 ± 3.4	3.10 ± 0.03	0.50 ± 0.06	1210 ± 98	7.1 ± 1.5
	W9	23.1	950	1.21	786 ± 2.3	1830 ± 2.8	–	–	–	–
	W10	23.1	990	1.26	793 ± 2.5	1814 ± 3.4	3.17 ± 0.12	0.40 ± 0.08	1150 ± 92	10.5 ± 1.8
	W11	18.1	900	1.47	741 ± 2.6	1741 ± 3.5	3.42 ± 0.05	0.77 ± 0.07	1082 ± 72	11.0 ± 2.1
	W12	20.5	900	1.29	767 ± 4.9	1797 ± 3.9	3.18 ± 0.05	0.65 ± 0.10	1099 ± 82	12.1 ± 2.6
	W13	25.3	900	1.15	779 ± 3.8	1810 ± 2.3	2.88 ± 0.04	0.50 ± 0.04	1160 ± 92	10.4 ± 1.9
		Hydrogen flow rate [l·min ⁻¹]	Oxygen flow rate [l·min ⁻¹]							
DJ-2600 ^a	DJ1	634	230	0.38	643 ± 0.5	1879 ± 1.5	3.06 ± 0.08	0.43 ± 0.10	1375 ± 96	7.8 ± 1.0
	DJ2	634	260	0.42	662 ± 0.6	1874 ± 2.0	–	–	–	–
	DJ3	634	270	0.44	665 ± 1.9	1878 ± 4.7	–	–	–	–
	DJ4	634	280	0.45	666 ± 1.0	1890 ± 1.8	2.88 ± 0.01	0.40 ± 0.11	1355 ± 89	5.4 ± 0.9
	DJ5	600	230	0.40	632 ± 0.7	1867 ± 2.2	3.14 ± 0.06	0.50 ± 0.06	1339 ± 106	3.7 ± 0.6
	DJ6	600	280	0.48	659 ± 1.9	1840 ± 2.8	3.05 ± 0.03	0.43 ± 0.05	1321 ± 98	3.5 ± 0.5
	DJ7	614	300	0.50	668 ± 1.9	1831 ± 2.6	–	–	–	–

^a Air flow rate: 343 [l·min⁻¹].

normal position of the substrate during spraying with Wokajet-400 and DJ-2600 respectively.

2.2. Characterization

The coating microstructure was examined by means of a scanning electron microscope (SEM, Jeol JSM-5600). Observations were carried out on polished cross-sections normal to the surface. The porosity of the coatings was evaluated by image analysis technique (Leica Qwin) using a Leica optical microscope. The coatings surface roughness (R_a) was measured by a Taylor–Hobson roughness tester.

The coatings microhardness was measured by using a Duramin 5 microhardness tester (Struers) with a Vickers diamond indenter under a load of 300 g, according to ASTM E384 standard. Fifteen data points were collected and averaged for each hardness value. Tribological evaluation of coated substrates under dry conditions was evaluated using a ball on disc tribometer (CSM Instruments), according to ASTM wear testing standard G-99. Samples were prepared for wear testing by diamond grinding and polishing down to 1 μm diamond. The ball-on-disc tests were carried out by sliding a 6 mm WC-6 wt.% Co pin against the polished samples at a constant linear speed of 0.10 ms^{-1} , with an applied load of 30 N. When testing was completed (10^6 cycles), the amount of material loss was evaluated by measuring the cross sectional area of the wear tracks using a profilometer (Taylor–Hobson Form Talysurf Plus roughness tester). At least three different tests were conducted for each test conditions and material.

3. Results and discussion

3.1. Influence of spray conditions on the particle in-flight properties

Two clear regions of different temperature and velocity arise from the use of different fuels as presented in the Fig. 1a. The operating range of the gas flows and fuel to oxygen ratios was quite different for the two mixtures (see Table 1). The kerosene–oxygen mixtures typically resulted in a greater velocity and a lower temperature of the particles than the hydrogen–oxygen mixtures [6–8]. It is important to note that the Wokajet-400 gun works with a combustion chamber pressure higher (7.5 bars) than DJ2600 gun (6.2 bars)[9]. Fig. 1b shows the evolution of the velocity and temperature of the powder sprayed with the DJ2600 gun. The particle velocity presents an increase vs. the oxygen flow rate, which corresponds to the fact that the total gas flow rate was also increased, leading to an increase in the gas velocity. The evolution of the particle temperature varies from 1874°C to 1890°C . The flame temperature reaches a maximum value near the 0.45 stoichiometric combustion ratio and decreases for higher values (Table 1) [9].

Fig. 2 shows a more detailed diagnostic study from altering the oxygen/fuel ratio using the Wokajet-400 gun. Fig. 2a shows that, increasing the total gas flow rate, initially both the particle velocity and the temperature increased. Nevertheless, from a certain oxygen flow rate value, a temperature decrease is observed, although the particle velocity continues increasing. First, the temperature evolution can be justified by the kerosene/oxygen proportion in the combustion reaction. The flame temperature reaches a maximum value, when the

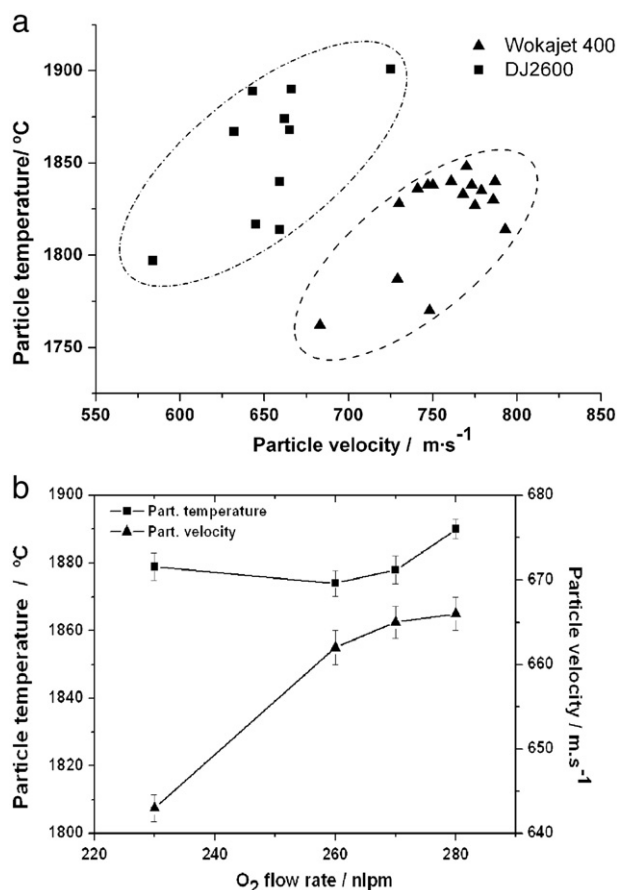


Fig. 1. (a) Evolution of particle temperatures and velocities for two fuel/oxygen mixtures; (b) Effect of the oxygen content on the velocity and temperature of particles sprayed with the DJ2600 gun, while maintaining constant hydrogen flow of 634 nlpm (normal litres per minute).

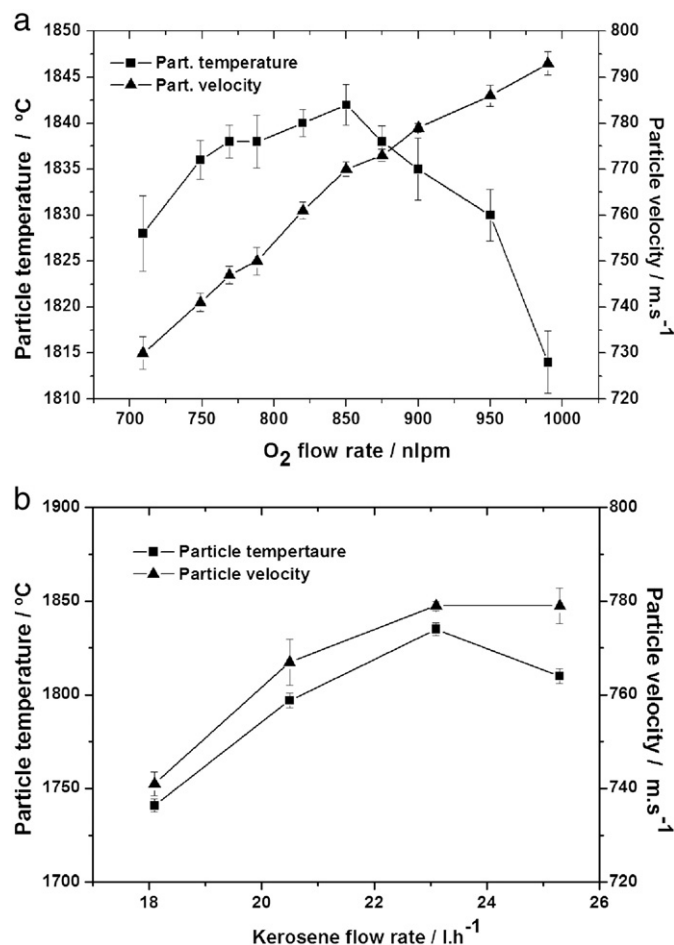


Fig. 2. (a) Effect of the oxygen content on the velocity and temperature of particles sprayed with the Wokajet-400 gun, while maintaining constant kerosene liquid flow of 23.1 l.h^{-1} ; (b) effect of the kerosene content while maintaining a constant oxygen flow of 900 nlpm (normal litres per minute).

oxygen content is enough to produce the complete combustion of kerosene. For higher oxygen flow rate values, there are an excess of oxygen that acts as cooling gas and consequently promotes a flame temperature decrease. However, liquid fuel HVOF guns generally operate with excess oxygen in order to prevent the formation of carbon deposits in the combustion chamber [9]. Secondly, the increase in total gas flow rate increases the particle velocity, reducing the residence time of the particle into the flame, and consequently decreasing the particle temperature. For an oxygen flow rate higher than 850 nlpm, the particle temperature decreases, together with the flame temperature and the shorter time of interaction with the jet. This explanation also justifies the evolution of temperature and velocity in Fig. 2b. On the other hand, the particle velocity presents a quasi linear increase vs. the oxygen flow rate, this corresponds to the fact that the total gas flow rate was also increased, leading to an increase in the gas velocity.

3.2. Particle velocity and temperature effect on coating properties

There are no significant differences in the microstructure of the coatings sprayed in the different conditions. The WC particles are distributed uniformly in the dense coatings (Fig. 3a). Fig. 3b shows a microstructure detail of coating sprayed with the DJ2600 gun, where one can observe the presence of some WC particles with rounded edges associated with partial dissolution of WC particles into the binder phase produced in-flight during the HVOF thermal spray process. As consequence, the Co–Cr binder matrix exhibits different grey shades. Regions of higher brightness are associated with a higher

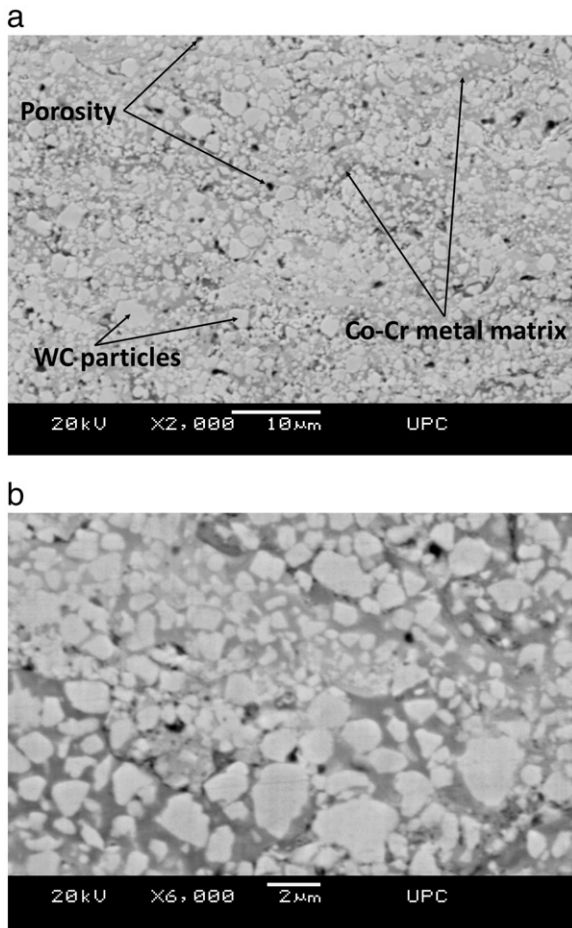


Fig. 3. (a) BSE micrograph of a transversal polished section of the HVOF WC-CoCr coating (Wokajet-400); (b) BSE image showing microstructure detail of the WC-CoCr coating (DJ2600).

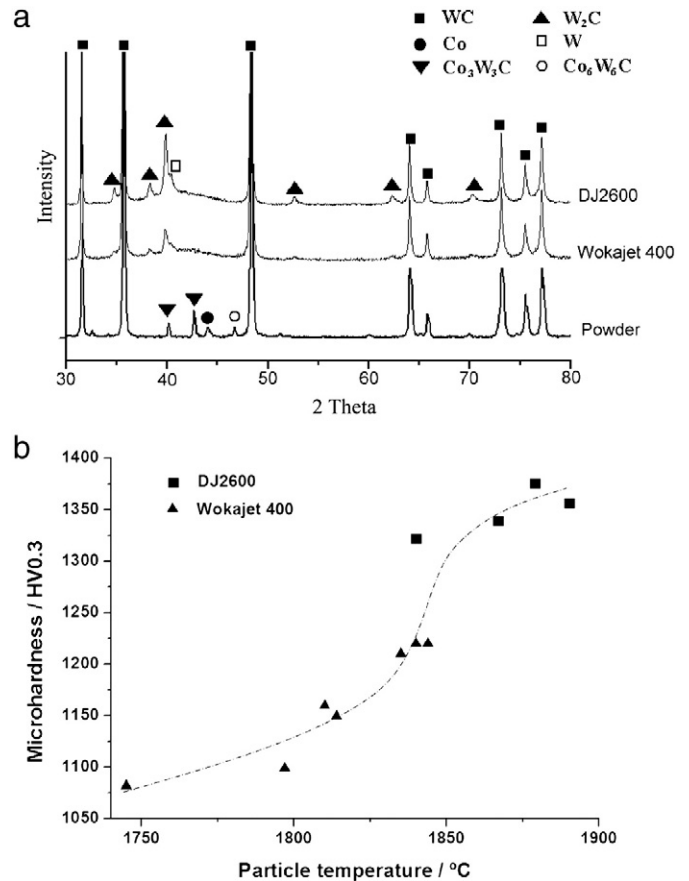


Fig. 4. (a) XRD diffraction patterns of the WC-CoCr powder and HVOF coatings; (b) Influence of the particle temperature on the coating hardness.

dissolution of W and C into the metallic binder phase [10,11]. Following impact, new phases will precipitate from the supersaturated binder phase, forming W₂C layers around existing WC particles [10,11]. The development of the W₂C phase can be observed in the XRD patterns (Fig. 4a). It is well-known that the formation of W₂C is largely dependent on the heating degree of the powders [12]. One can notice, with hydrogen there was a greater degradation of the monocarbide WC phase during the thermal spraying step in comparison with kerosene. This fact is due to that hydrogen provides higher particle temperatures and lower velocities than kerosene. Furthermore, it has to consider that in the DJ-2600 gun the powder is injected directly into the combustion chamber, whereas in the Wokajet-400 gun the particles are injected behind the combustion chamber where the flame temperature is lower and the powder heating and acceleration only occurs in the barrel [6].

Effects of in-flight particle temperature and velocity on the deposited coating properties, i.e. porosity content, microhardness or wear rate are shown in Table 1. The surface roughness and level of porosity are related with the temperature and velocity of the agglomerates during spraying. Both characteristics decreased with an increase in spray particle temperature and an improvement in particle melting-degree. The combination of high temperature and velocity should facilitate the agglomerate deformation upon impact, so that the solidifying splats will be able to conform to the surface of the previously deposited layer and fill the pores and defects.

The influence of the particle temperature on the coating hardness can be seen in Fig. 4b. The microhardness of the coatings lies between 1082 and 1375 HV0.3 (see Table 1). In general, one can observe an increase in coating microhardness with rising the particle temperature. This fact is associated with the greater degree of decarburisation of WC particles with the temperature increase. This decarburisation

decreases the volume fraction of the WC carbides, but its detrimental effect on the hardness is compensated both by the dissolution of tungsten and carbide into the CoCr binder phase, which causes a hardness increase of the metallic matrix, and the presence in the coating of a higher level of W_2C phase. It is reasonable that the hardness increases with increasing content of W_2C in the coatings, because W_2C phase ($HV=3000$) is harder than the WC phase ($HV=1300\text{--}2300$) [2,12].

Finally, Table 1 shows the specific wear rate values for the studied coatings. The wear mechanism for WC-CoCr coatings is based on the combination of three mechanisms: the wear of individual WC particles, the falling out of particles in grooves and the spallation of entire splats [13]. These three mechanisms operate in all coatings to different degrees, depending on the coating properties that result from the processing parameters. There is no obvious relation between particle temperature and wear properties of deposited coatings. Nevertheless, one can observe a relation between the wear rate and the coating microhardness. The coatings sprayed with the Wokajet-400 gun show a clear tendency to a wear rate reduction with the hardness increase. Nevertheless, in the coatings sprayed with the DJ-2600 gun, although the hardness is higher than coatings sprayed with the Wokajet-400 gun, the increase of the presence of the hard W_2C phase surrounding the WC particles, together with an embrittlement of the matrix as consequence of an enrichment of the CoCr metallic binder phase in W and C (due to decarburization of WC particles) cause a reduction of the bonding of the WC particles with the metallic phase, favouring an increase of the abrasive wear mechanism [14,15]. Microscopic observation of the wear tracks provides further information about the wear mechanisms and their relation to coating properties. In the coatings sprayed with the DJ-2600 gun, one can observe that the wear track exhibited more significant pitting and delamination with the hardness increase. Other authors have noted that the sliding wear rate of sprayed coatings increased with increasing levels of decomposition product, especially W_2C [7,13,15–17].

4. Conclusions

In this study, the influence of spray parameters on the particle in-flight temperature and velocity during HVOF-spraying of WC-CoCr powder was investigated by on-line particle monitoring.

The kerosene–oxygen mixtures resulted in a greater velocity and a lower temperature of the particles than the hydrogen–oxygen mixtures.

The oxygen flow rate affects the combustion reaction, but an excess of oxygen will cool the flame decreasing the particle temperature. Furthermore, the increase in total gas flow rate increases the particle velocity, reducing the residence time of the particle into the flame, concerning a decrease in the particle temperature.

For both fuels, the amount of porosity and surface roughness tended to decrease with increasing the particle temperature and velocity. Moreover, the results indicate that the coating microhardness tends to increase with increasing particle temperature, as consequence of higher presence of the harder W_2C phase. In the coatings sprayed with the Wokajet-400 gun, one can observe a clear tendency to a wear rate reduction with the hardness increase. Nevertheless, in the coatings sprayed with the DJ-2600 gun, the wear resistance is related to the carbide degradation and particle temperature.

Acknowledgements

The authors wish to express their gratitude to Spain's Ministerio de Ciencia e Innovación for its financial support under project no. MAT2008-01261 and GUTMAR S.A. company for the support in this work.

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