

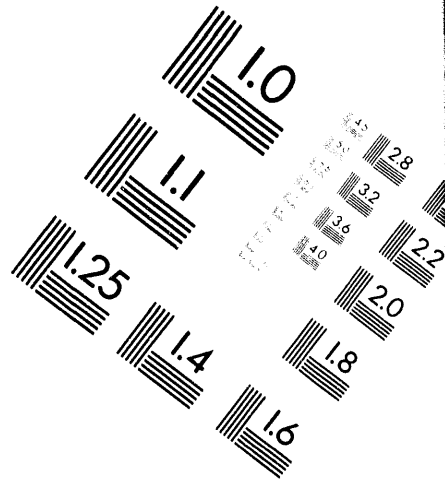
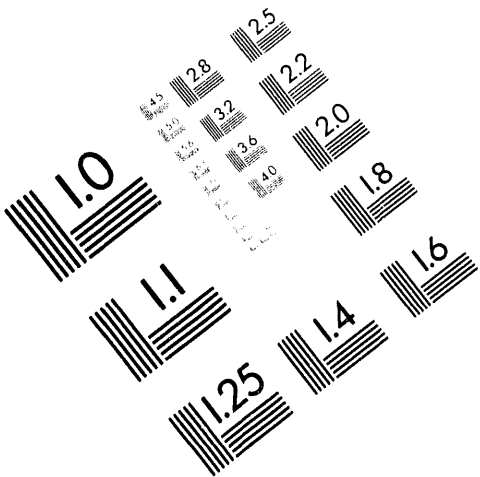


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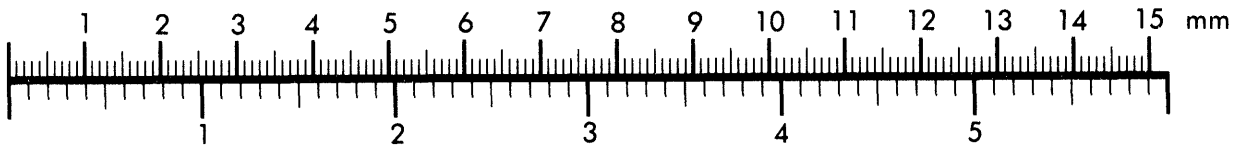
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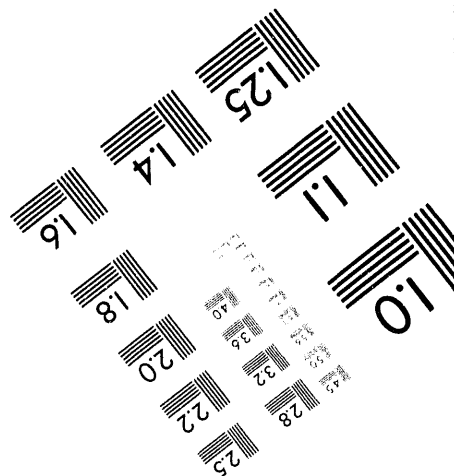
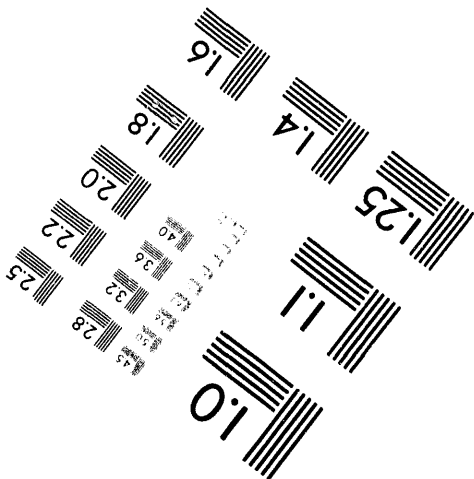
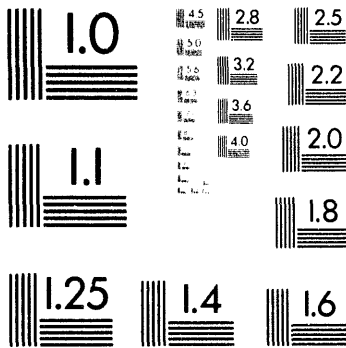
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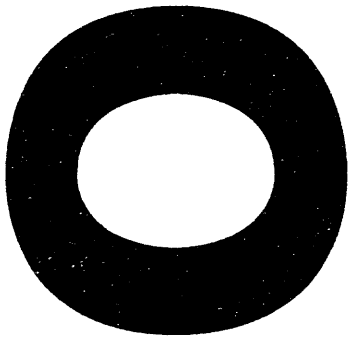
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CORROSIVE EFFECTS OF SUPERCRITICAL CARBON DIOXIDE AND COSOLVENTS ON METALS*

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ABSTRACT

With the eventual phase-out of chlorofluorocarbons, and restrictive regulations concerning the use of cleaning solvents such as hydrochlorofluorocarbons, and other volatile organic compounds, it is essential to seek new, environmentally acceptable cleaning processes. In the DOE Complex and in industry, an environmentally sound process for precision cleaning of machined metal parts is one of the issues that needs to be addressed. At Sandia, we are investigating the use of supercritical carbon dioxide (CO₂) as an alternative cleaning solvent for this application. Carbon dioxide is nontoxic, recyclable, and relatively inexpensive. Supercritical CO₂ has been demonstrated as a solvent for many nonpolar organic compounds, including hydrocarbon-based machining and lubricating oils. The focus of this work is to investigate any corrosive effects of supercritical CO₂ cleaning on metals.

Sample coupons of several common metals were statically exposed to pure supercritical CO₂, water saturated supercritical CO₂, and 10 wt% methanol/CO₂ cosolvent at 24,138 kPa (3500 psi) and 323°K (50°C) for 24 hours. Gravimetric analysis and magnified visual inspection of the coupons were performed before and after the exposure tests. Electron microprobe, x-ray photoelectron spectroscopy (XPS), and Auger electron surface analyses were done as needed where visual and gravimetric changes in the samples were evident. The results of these experiments will be reported.

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INTRODUCTION

Cleaning solvents such as chlorofluorocarbons (CFCs) and, more recently, hydrochlorofluorocarbons (HCFCs) are being used in industry and the DOE weapons complex for the removal of machining and lubricating oils from machined metal parts in precision cleaning processes; that is, the cleaning of precisely machined metal surfaces to extremely low levels of surface contamination. With the eventual phase-out of ozone-depleting CFCs as dictated by the Montreal Protocol international environmental treaty, and with increasingly restrictive regulations concerning the use of cleaning solvents such as HCFCs and other volatile organic compounds, environmentally sound alternatives need to be identified.

As part of the DOE's effort to find suitable substitutes for environmentally objectionable solvents, Sandia National Laboratories is investigating the feasibility of using supercritical carbon dioxide (CO₂) to clean machining oils from metal parts¹. Supercritical carbon dioxide can be simply defined as carbon dioxide which exists above its critical temperature, $T_c = 304.1^\circ\text{K}$ (31.1°C), and pressure, $P_c = 7386 \text{ kPa}$ (1071 psi). The supercritical region on a CO₂ pressure-temperature phase diagram is shown in Figure 1². Supercritical CO₂ exists as a single phase and can be considered to be a dense gas, but possesses both liquid-like and gas-like properties that are advantageous for the dissolution and cleaning of nonpolar organic compounds. Supercritical CO₂ has solvating properties similar to those of organic solvents, and depending on pressure and temperature conditions, can have densities approaching those of liquid solvents. Furthermore, the solvating power of supercritical fluids tends to increase with density as liquid-like molecular interactions become more prevalent³. Supercritical CO₂ exhibits gas-like properties of diffusivity and viscosity which enhance its ability to transport solubilized contaminants away from a substrate being cleaned.

Obviously, an important prerequisite is that the materials to be removed from the substrate must be soluble to some extent in the supercritical fluid. In fact, carbon dioxide has been demonstrated as a good solvent for many organic compounds⁴, including some hydrocarbon-based machining oils^{5,6}. Although many polar and ionic compounds show little or no solubility in pure CO₂, low concentrations of polar solvents (e.g., methanol, water) may be added to the CO₂ to greatly enhance the solubility of the contaminant. A second requirement is that the substrate to be cleaned must be compatible with the cleaning medium. Aside from anecdotal evidence, there appears to be no extensive published research on the compatibility of metals with supercritical CO₂ with respect to corrosion. It is for this reason that our research into the compatibility of selected metals with supercritical CO₂ and cosolvents is being reported.

EQUIPMENT

A schematic diagram of the 5000 psi carbon dioxide pressure system used in our corrosion compatibility experiments is presented in Figure 2. Two size 2 technical grade carbon dioxide (99.5% min. purity) cylinders (TriGas, Inc., Albuquerque, NM) serve as the CO₂ source. Two pneumatic Gas Booster compressors (Haskel, Inc., Burbank, CA) are used to achieve the supercritical pressures required for our tests. The CO₂ cylinders and compressors are arranged in series such that the first cylinder and compressor maintain the second cylinder at approximately 5862 kPa (850 psi), which is the saturation pressure for CO₂ at room temperature. The second cylinder and compressor, in turn, pressurize the temperature-controlled sample vessel to the desired working pressure. We have found that this two-stage compressor arrangement permits greater consistency in CO₂ delivery to the sample vessel. Our experience has shown that as pressure in the system supply cylinder decreases significantly below the saturation pressure, the compressor behaves more erratically with occasional hesitation and surging. Maintaining the system supply cylinder at constant pressure avoids this behavior. The sample vessel is a 1800 ml 316SS reactor vessel (Parr Instrument Co., Moline, IL). The body of the sample vessel is immersed in a temperature controlled water bath in order to maintain the desired working temperature. Temperature is monitored through a thermocouple well in the vessel lid which extends down into the body of the vessel. The exit line from the sample vessel leads to a pneumatically controlled vent valve which is opened when the system is depressurized. The vent line leads to a 1000 ml 316SS recovery vessel (Parr Instr. Co.) where a majority of the cosolvent, if any, would be deposited since it would be less soluble in CO₂ at decreased pressure during venting. The vent line terminates in a fume hood which exhausts the CO₂ gas out of the laboratory. All tubing in the system is 316 stainless steel with 0.635 cm (1/4 in) outside diameter and 0.165 cm (0.065 in) wall thickness.

In order to insure that the source gas is dry, a vessel packed with one-half Drierite desiccant and one-half molecular sieve was installed upstream of the sample vessel. Since pump-type compressors invariably generate particulates, 0.5 μm porous stainless steel filters are in-line after the first stage compressor and after the desiccant/molecular sieve vessel, also capturing any particulate generated by the second stage compressor.

There are several safety related items designed into the system. To protect against inadvertent overpressurization, pressure safety relief valves were installed at both CO₂ cylinders, and also on the pressure tubing leading to the sample vessel. Both sample and recovery vessels were purchased with rupture discs installed. The pneumatic compressors have check valves built-in to avoid back flow of CO₂ from the sample vessel to the source cylinders. To serve as a back up, an in-line check valve was installed between the system supply compressor and sample vessel.

EXPERIMENTAL SECTION

BACKGROUND INFORMATION

The temperature and pressure conditions used in our testing were 24,138 kPa (3500 psig) at 323.0°K (50.0°C). These conditions were chosen since they comfortably exceed the critical point of CO₂, and could reasonably be used in an actual supercritical CO₂ cleaning process. The normal exposure time was chosen at 24 hours, significantly longer than an actual cleaning cycle, which is likely to be in the time frame of minutes. If corrosion is not seen in a 24 hour exposure test, it is reasonable to assume that it will not occur in a cleaning process of much shorter duration.

Corrosion compatibility testing of metals was performed in pure supercritical CO₂, and in two cosolvent systems: deionized water-saturated supercritical CO₂, and 10 wt% methanol (certified A.C.S., Fisher Scientific, Fair Lawn, NJ) in supercritical CO₂. Under our test conditions, water is soluble at approximately 0.3 wt%⁷. Since this solubility is quite low, we chose to fully saturate the CO₂ to insure that water existed in the vapor phase at its maximum solubility level. Therefore, during the water-saturated CO₂ exposure experiments, water-saturated CO₂ vapor phase coexisted with a small amount of CO₂-saturated liquid water phase at the bottom of the sample vessel. From the CO₂ density (0.83 g/ml) at 24,138 kPa (3500 psi) and 323.0°K (50°C) and the sample vessel volume (1800 ml), it was calculated that about 5 grams of water will dissolve at a 0.3 wt% solubility level. Approximately 40 grams of deionized water was added to the sample vessel in the water-saturated CO₂ tests to insure maximum solubility. Methanol, on the other hand, is very soluble in supercritical CO₂. From experiments we conducted and from other experimental data, it is clear that the equilibrium solubility of methanol in CO₂ far exceeds 10 wt% at our test conditions^{8,9}. This concentration was chosen since it is already at a higher level than is likely to be used in an actual cleaning process using methanol as an organic solvent modifier. It was calculated that 175 grams of methanol must be added to the vessel to make a 10 wt% solution of methanol in CO₂ at the test conditions.

Prior to beginning the actual compatibility testing, precleaning of the pressure system was done with a combination of manual cleaning and repeated flushing with CO₂. Gravimetric analysis and scanning Auger surface analysis performed on metal samples exposed to supercritical CO₂ in the system indicated cleanliness to less than 1 µg/cm² surface contamination.

In determining which metals would be tested for compatibility with supercritical CO₂ and cosolvents, it was decided that several common engineering metals would be screened, and other more exotic alloys could be tested later if desired. The metals chosen for corrosion testing in this work are as follows:

- Stainless steel (grades 304L and 316)
- Aluminum (grades 2024, 6061, and 7075)
- Copper (grade CDA 101)
- Carbon steel (grade 1018)

The metal coupons (Metal Samples Co., Munford, AL) were 50.8 mm (1.80 in) long x 25.4 mm (1.00 in) wide x 0.25 mm (0.010 in) thick, except for the aluminum coupons which were 0.50 mm (0.020 in) thick. A 3.18 mm (0.125 in) diameter hole at one end serves to hang the coupons from a glass stand inside the test vessel.

Although carbon steel would not be a likely choice for applications where corrosion is a possibility, especially with long-term viability issues concerning weapons applications, we decided to look at C1018 since there seemed to be a good possibility that some oxidation of the metal might occur in the presence of water. Stainless steels, on the other hand, are formulated to be corrosion resistant steels, aluminum creates a passivating air-formed oxide layer, and copper, due to its atomic structure, is considered to be a "noble" (i.e., corrosion resistant) metal¹⁰. The corrosion resistance of these metals in the presence of supercritical fluids may be somewhat less predictable.

EXPERIMENTAL PROCEDURE

Some sample preparation and inspection was done prior to supercritical exposure. All coupons were precleaned to remove surface contaminants including a protective inhibitor coating that the manufacturer applies to the metal surfaces for shipping. The precleaning consisted of manual wet abrasion of the metal surfaces with 600 grit silicon carbide paper and deionized water, followed by a five minute degreasing with 1,1,1-trichloroethane to remove any nonpolar contaminants, blown dry with ultra-high purity (UHP) nitrogen, and a five minute degreasing with isopropanol to remove polar contaminants, also blown dry with UHP nitrogen. Both sides of all samples were then photographed at 4x magnification, and at least one higher magnification (33x) photo was taken of one sample for each alloy to document their visual appearance prior to the corrosion testing. After photography, the coupons were weighed to the nearest microgram (μg) on a Mettler M3 microbalance in order to get an accurate pre-test sample weight. Tweezers were used to manipulate the samples during cleaning and in all handling thereafter.

The coupons were suspended from a glass stand consisting of a vertical rod with a base supporting horizontal arms on which the coupons were hung. Generally, three samples of one type of metal were tested at a time, and care was taken to keep coupons from sticking together so that all surfaces were exposed to supercritical fluid. The deionized water or methanol cosolvent, if any, was added to the vessel which was preset at the working temperature of 323.0°K (50°C), and the glass stand with coupons was placed inside. The vessel was sealed and pressurized with CO₂ to the working pressure of 24,138 kPa (3500 psig). The samples were maintained at the test pressure and temperature for a period of 24 hours. After the 24 hour exposure time, the system was depressurized, the sample vessel was opened, and the glass stand with coupons was removed. When methanol cosolvent was used in corrosion testing, any residual methanol tended to evaporate from the samples within seconds after they were removed from the vessel. After the deionized water cosolvent tests, the coupons were uniformly wet with tiny droplets of water, which were carefully dabbed dry with clean kimwipes, and then blown with UHP CO₂. The samples were rephotographed and reweighed after the supercritical exposure. Pre-test and post-test photographs were compared to look for visual changes, and any weight changes were normalized per unit area (i.e., $\mu\text{g}/\text{cm}^2$) and then averaged. Further analysis was done on test samples where significant weight and/or visual changes were evident. Electron microprobe, Auger electron spectroscopy (AES), x-ray photoelectron spectroscopy (XPS), or a combination of these surface analyses was done as deemed necessary.

RESULTS AND DISCUSSION

Corrosion compatibility testing was completed for all metals mentioned previously in pure supercritical CO₂, deionized water-saturated supercritical CO₂ cosolvent, and 10 wt% methanol/supercritical CO₂ cosolvent at our standard test conditions of 24,138 kPa (3500 psig) at 323.0°K (50.0°C) for a period of 24 hours. Results of gravimetric analysis and comments on visual changes in samples are shown in Table 1.

There was no evidence of corrosive attack caused by pure supercritical CO₂ on any of the metals tested. No visible signs of corrosion were observed on any of the samples, and normalized weight changes were generally within about 1 $\mu\text{g}/\text{cm}^2$ or less, which were considered to be insignificant. Unfortunately, accurate gravimetric analysis for 1018 carbon steel could not be obtained in pure supercritical CO₂ testing or in the cosolvent experiments. Unstable weight measurements for C1018 may be related to the fact that it was the only magnetic metal tested. It is believed the magnetic properties of the steel may have caused instabilities on the microbalance. Attempts to degauss the coupons did not eliminate the instabilities.

Corrosion tests performed in water-saturated CO₂ failed to cause any corrosive attack on the stainless steels, aluminums, and copper. Aside from a few random water spots from incidental splashing, no visual changes were evident and weight changes were insignificant for these metals. Water-saturated CO₂ exposure did, however, cause visually obvious signs of corrosion on 1018 carbon steel. Uniformly distributed discolorations in the form of light brown spots completely covered the surfaces of the C1018 samples. A comparison of C1018 before and after water-saturated CO₂ exposure is shown in Figure 3. Electron microprobe elemental analysis was performed which indicated, aside from the alloying elements of iron and carbon, significant oxygen enrichment in the discolored areas on the sample surface. This was interpreted as further evidence of oxidation taking place on C1018 due to water-saturated CO₂ exposure. To determine the corrosive effects of water in the absence of CO₂ on C1018, several samples were placed in the sample vessel and exposed to water-saturated air at 323°K (50°C) and ambient pressure for 24 hours exposure time. Magnified visual inspection after the test showed no signs of corrosive attack on C1018. From these results, it appears that CO₂ enhanced the corrosive effects of water on the carbon steel in the cosolvent test, most likely because carbonic acid is formed in the supercritical CO₂/water environment.

The 304L and 316 stainless steel alloys, and 1018 carbon steel were unaffected by exposure to the supercritical cosolvent of 10 wt% methanol in CO₂. All samples were visually unchanged based on post-test inspection, and

gravimetric data acquired for the stainless steels indicated virtually no weight change. But after completing the 24 hour exposure of CDA 101 copper at our standard pressure and temperature conditions, it was obvious that corrosion had taken place due to supercritical methanol/CO₂ exposure. The surfaces of the copper samples had a darkened, tarnished appearance, and the average weight loss relative to previous testing was tremendous at -20.79 μg/cm². In order to determine the relationship of exposure time to average weight change, experiments were conducted in which the standard pressure and temperature conditions were held constant, and exposure time was varied from 4 hours up to 49 hours. The copper sample weight tended to decrease (i.e., average weight loss increased) with increasing exposure time. The weight loss results of this time study are shown graphically in Figure 4. Furthermore, the tarnish on the surface of the copper tended to appear darker with increasing exposure time. Figure 5 shows a comparison of surface appearances of an unexposed CDA 101 copper sample with samples exposed to supercritical methanol/CO₂ for 16 hours and 49 hours. Scanning Auger surface analysis was done on a CDA 101 sample exposed for 16 hours to the cosolvent, which showed little change except for a small increase in oxygen on the test sample (11% oxygen) compared to an unexposed control sample (7% oxygen). Since this seemed to be a rather small elemental change considering the significant weight change and tarnishing of the test samples, XPS analysis was performed on a copper sample exposed to supercritical methanol/CO₂ for 40 hours in an attempt to identify the composition of any corrosion products remaining on the sample surface. The XPS results were consistent with the previous Auger analysis in that the elemental analysis of the test sample showed little change after supercritical exposure. There was essentially no change in oxygen content, with 20.8% oxygen in the control sample compared to 20.6% oxygen in the test sample. Figure 6 shows the Cu LMM (i.e., Auger emission) energy peaks from the XPS spectra for a sample exposed to methanol/CO₂ for 40 hours and for an untreated control sample. The untreated sample yielded two peaks closely together at binding energies of 567.5 eV indicating elemental copper and 569.5 eV indicating cuprous oxide (Cu₂O). This implies that a very thin Cu₂O layer exists on the unexposed copper substrate. The supercritically exposed sample gave a single Cu₂O peak at 569.5 eV with a small shoulder in the energy range of elemental copper. These results indicate that the oxide layer is very slightly thicker on the exposed sample, since the Cu₂O peak nearly masks the copper peak, but no other corrosion products were seen other than Cu₂O which is also on the untreated control sample. It is believed that very slight differences in the thickness, and possibly the structure, of the oxide on the copper substrate may be responsible for the differences in tarnished appearance. While this corrosion process warrants further study, the marginal oxide layer and the absence of unique reaction products, combined with significant loss of copper from test samples seem to indicate a process similar to the chemical dissolution of copper.

Compatibility testing of the three aluminum alloys (2024, 6061, and 7075) in 10 wt% methanol/CO₂ supercritical cosolvent gave varied results. No corrosive attack was apparent on Al 6061 and Al 7075 test samples, since no significant visual changes were noted and weight changes were negligible with average gains of 0.31 μg/cm² and 0.25 μg/cm² respectively. However, Al 2024 did experience corrosion with uniform black spotting on the sample surfaces and significant average weight gain of 26.68 μg/cm². A sample of Al 2024 after 24 hours exposure to the methanol/CO₂ cosolvent, compared to an unexposed sample, is shown in Figure 7. Electron microprobe analysis of the affected areas on Al 2024 showed the dark regions to be small masses of material adhering to the metal surface. The analysis indicated that the corrosion product consists primarily of aluminum and oxygen, indicating an aluminum oxide, with minor amounts of other alloying elements of 2024. It is believed that the corrosion of Al 2024 and not of 6061 and 7075 may be explained by the composition of the three alloys. All contain small amounts of chromium, iron, manganese, magnesium, and silicon as alloying elements, but 2024 contains about 4.5% copper, while copper is present only at about 0.3% and 1.5% in 6061 and 7075 respectively. With Al 2024 in a corrosive environment, it is not uncommon to have a galvanic corrosion reaction in which precipitated copper acts as a cathode and the aluminum matrix as an anode, with the resulting current causing intercrystalline corrosion of the aluminum¹¹.

CONCLUSIONS

Supercritical carbon dioxide and cosolvents may potentially be used as cleaning media for removing contaminants from metallic substrates. Compatibility of the metal with the supercritical fluid is an important consideration when formulating a cleaning process. Corrosion testing of stainless steels (304L and 316), aluminum alloys (2024, 6061, and 7075), copper (CDA 101) and carbon steel (1018) was conducted in pure supercritical CO₂, water-saturated CO₂, and in the supercritical cosolvent of 10 wt% methanol/CO₂, all at 24,138 kPa (3500 psig) and 323.0°K (50.0°C) for a period of 24 hours. No signs of corrosion were observed on any of the metals when exposed to pure supercritical CO₂, therefore, all are believed to be fully compatible with CO₂ alone. Compatibility testing with water-saturated CO₂ indicated that only carbon steel 1018 experienced corrosive attack due to the supercritical

exposure, but all other metals were unaffected. Supercritical cosolvent exposure of 10 wt% methanol in CO₂ caused corrosion on both CDA 101 copper and on 2024 aluminum, but all the other metals proved to be compatible.

In the instances where corrosion was observed, an alternative cleaning medium should probably be chosen but it should be reiterated that our tests were conducted for 24 hour intervals, while for practical purposes, the duration of an actual cleaning process would be minutes rather than hours. Further study would be needed to determine if there is an acceptable amount of time in which these cosolvents could be used to clean the material without causing any adverse affects to the substrate.

ACKNOWLEDGEMENTS

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Table 1

Results of gravimetric analysis and magnified visual inspection of metal samples exposed to supercritical fluids in corrosion compatibility testing (**results indicating corrosion are in bold**).

Pure supercritical CO₂ exposure at 24,138 kPa (3500 psig) and 323.0°K (50.0°C) for 24 hours

Metal alloy	Avg. weight change (µg/cm ²)	Visual observations
304L SS	-0.87	no change
316 SS	-1.06	no change
Al 2024	+0.53	no change
Al 6061	+0.85	no change
Al 7075	+0.43	no change
C1018	not available	no change
CDA 101	+0.06	no change

Water-saturated supercritical CO₂ exposure at 24,138 kPa (3500 psig) and 323.0°K (50.0°C) for 24 hours

Metal alloy	Avg. weight change (µg/cm ²)	Visual observations
304L SS	+0.15	no change
316 SS	+0.77	no change
Al 2024	+0.74	no change
Al 6061	+1.85	no change
Al 7075	+1.31	no change
C1018	not available	brown oxide
CDA 101	+0.97	no change

10 wt% methanol/CO₂ supercritical exposure at 24,138 kPa (3500 psig) and 323.0°K (50.0°C) for 24 hours

Metal alloy	Avg. weight change (µg/cm ²)	Visual observations
304L SS	+0.06	no change
316 SS	+0.14	no change
Al 2024	+26.68	black oxide
Al 6061	+0.31	marginally less lustrous
Al 7075	+0.25	no change
C1018	not available	no change
CDA 101	-20.79	tarnished

Figure 1 - Pressure-Temperature phase diagram for carbon dioxide.

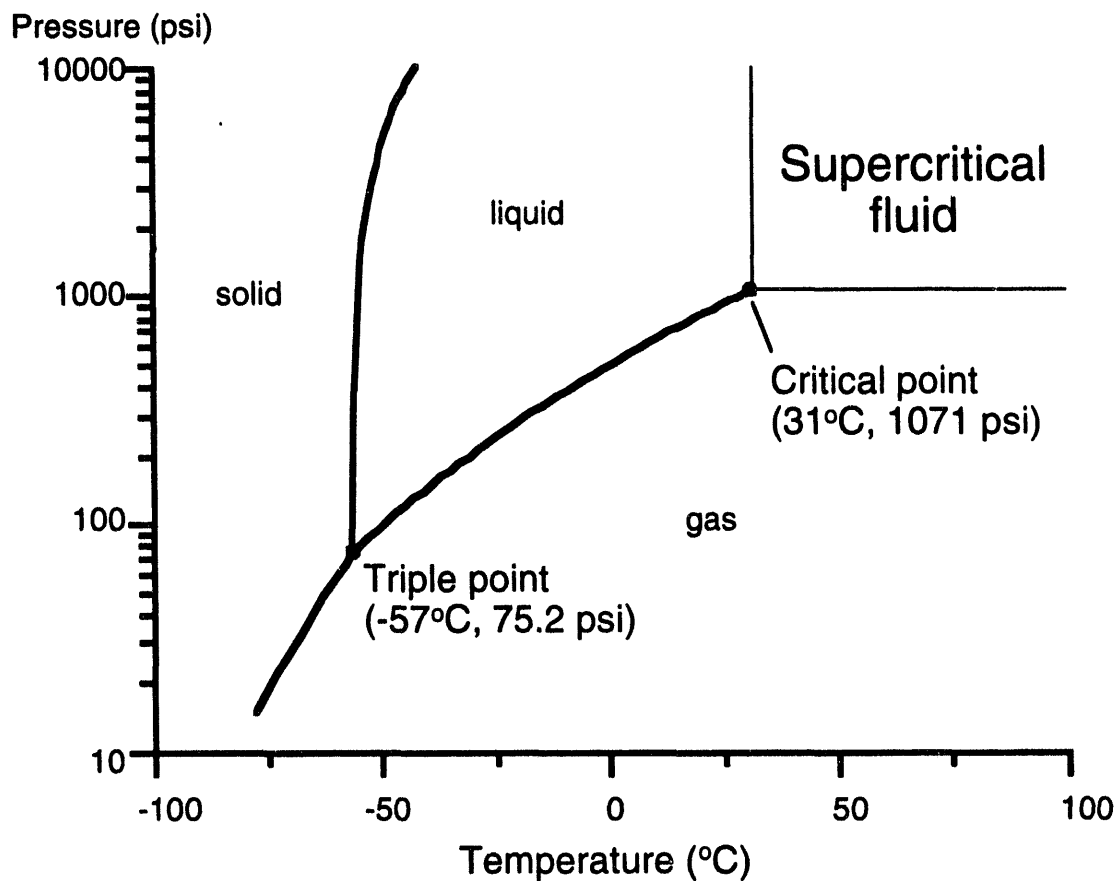


Figure 2 - Schematic drawing of the 5000 psi CO₂ pressure system used for corrosion testing.

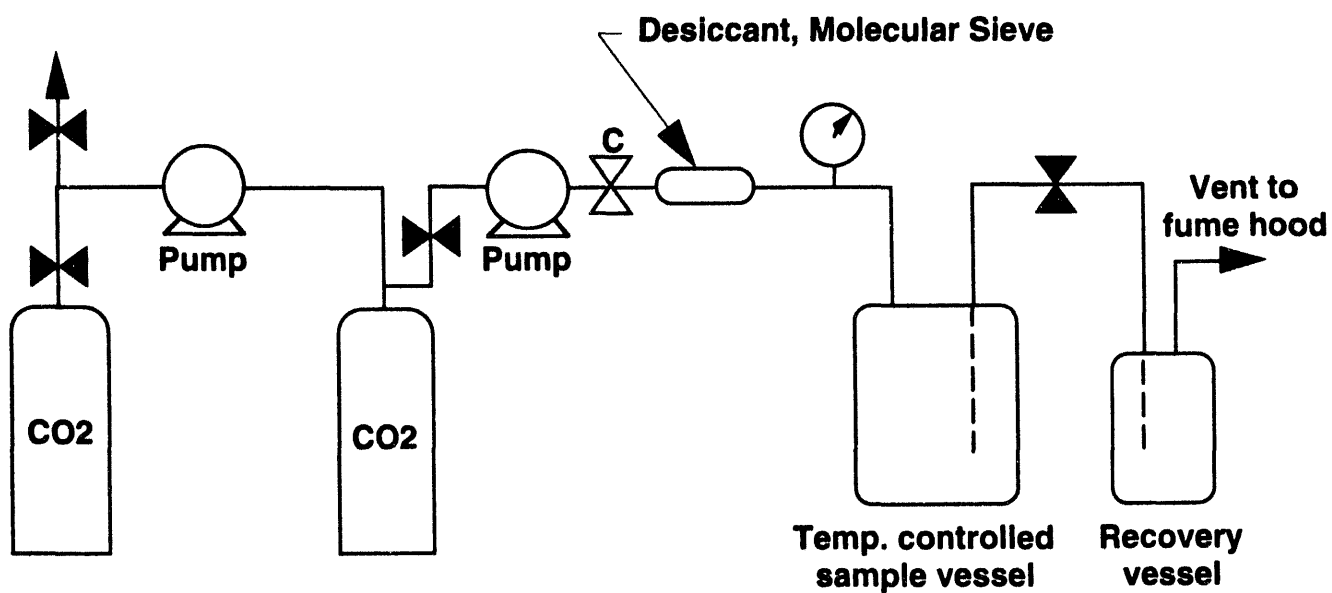


Figure 3 - C1018 before (left) and after (right) water-saturated supercritical CO₂ exposure at 24,138 kPa (3500 psig) and 323.0°K (50.0°C) for 24 hours.

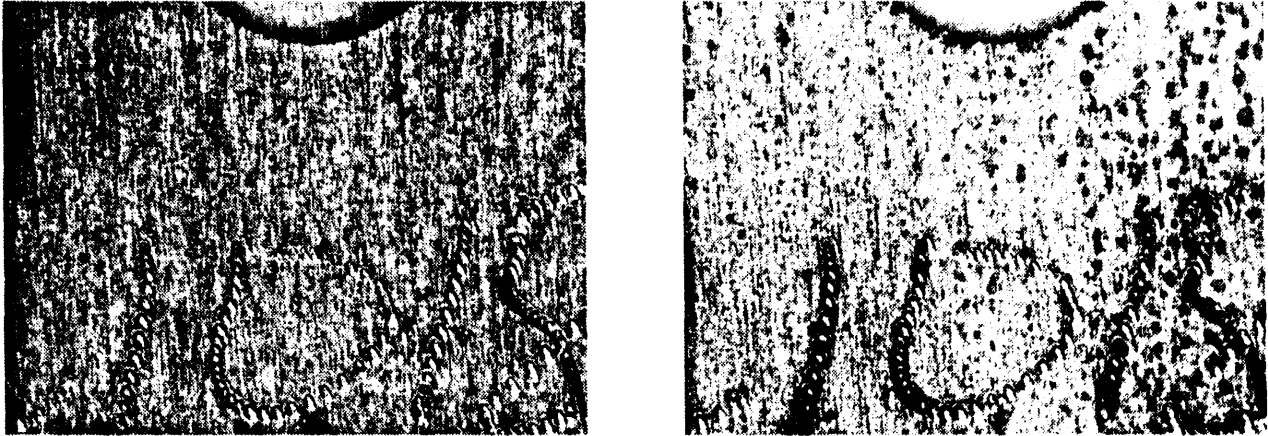


Figure 4 - Plot of CDA 101 copper weight change vs. exposure time to 10 wt% methanol in CO₂ at 24,138 kPa (3500 psig) and 323.0°K (50.0°C).

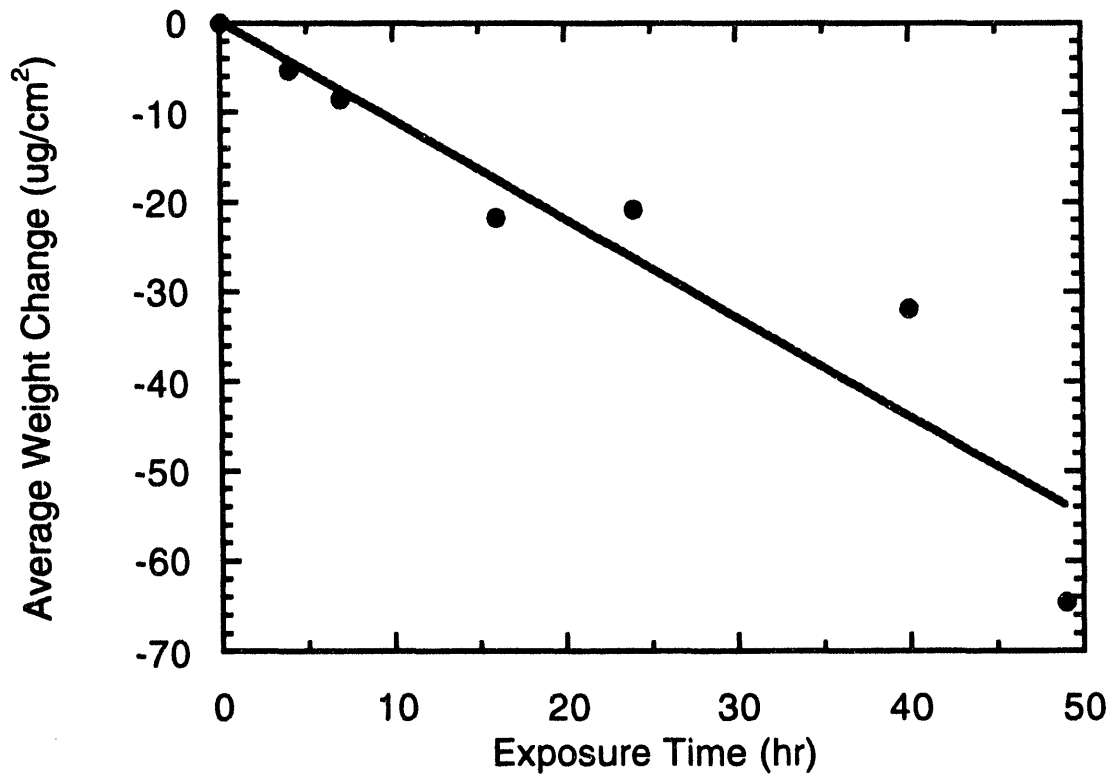


Figure 5 - Surface finishes of CDA 101 copper with no supercritical exposure (left), 16 hours supercritical exposure to 10 wt% methanol in CO₂ (center), and 49 hours exposure to the same supercritical cosolvent.

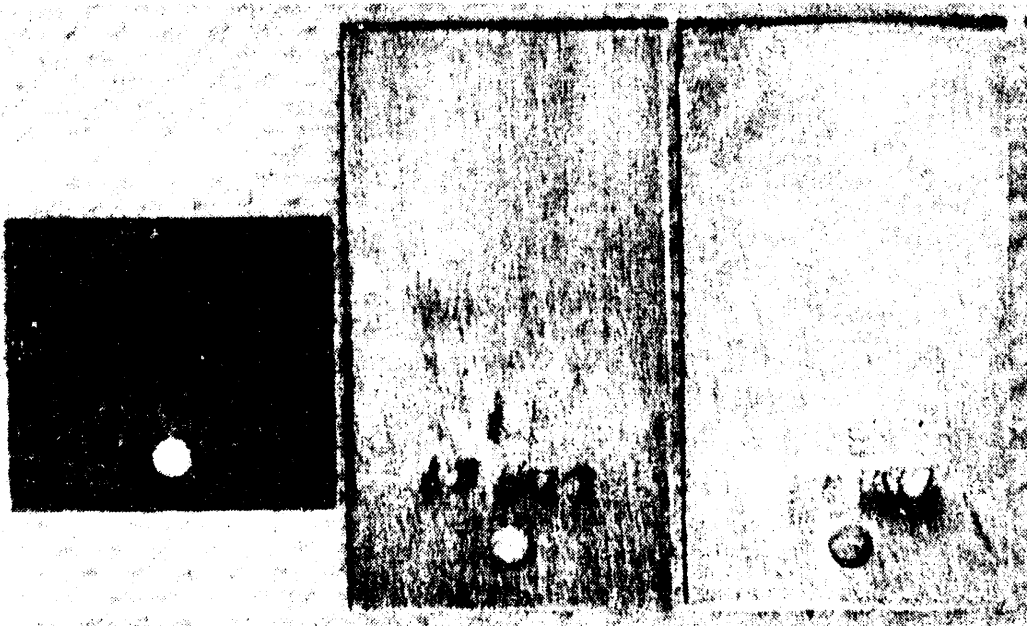


Figure 6 - Copper LMM energy peaks for an unexposed control sample and for a sample exposed to the supercritical cosolvent of 10 wt% methanol in CO₂ at 24,138 kPa (3500 psig) and 323.0°K (50.0°C) for 40 hours.

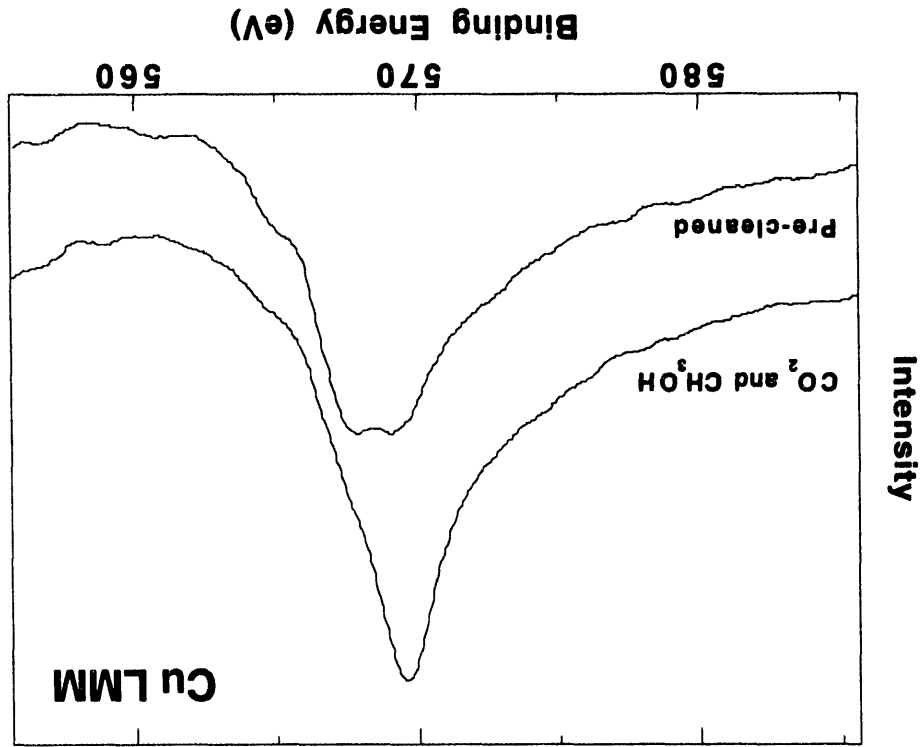
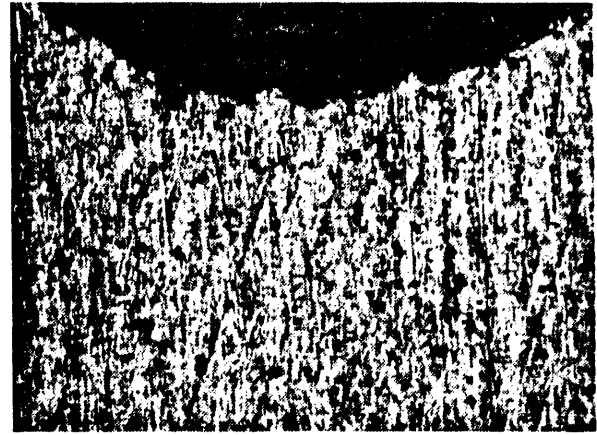
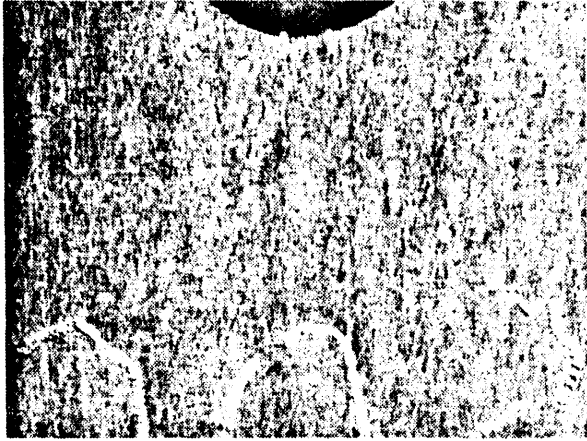


Figure 7 - Al 2024 before (left) and after (right) exposure to the supercritical cosolvent of 10 wt% methanol in CO₂ at 24,138 kPa (3500 psig) and 323.0°K (50.0°C) for 24 hours.



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