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How dry is dry? - A critical analysis of surface conditions used in dry metal forming

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Abstract

In the present study, the surface conditions of workpieces used for dry-metal forming experiments were analyzed. Specifically, the effectiveness of different cleaning approaches was evaluated using x-ray photoelectron spectroscopy, infrared spectroscopy and wetting experiments. The best cleaning results were obtained using a CO_2-based approach. CO_2 acts as an effective solvent and as a result of the mechanical impact, it removes material from the surface. In fact, cleaning results were similar to those achieved by plasma cleaning. However, even simple cleaning with a towel and acetone left only a surface film of less than 100 nm. A residual oil film thickness below 100 nm on the work piece appears sufficient to mimic true dry-forming conditions in most cases. In order to determine cleanliness of surfaces used in dry-metal forming, an infrared spectroscopy-based oil film gauge along with a customized extended calibration curve turned out to provide for sufficiently accurate data.

Keywords: cleaning, coating, lubricant, spectroscopy, surface analysis

1 Introduction

Metal forming processes that avoid lubricants could provide for both economic as well as ecological advantages. As detailed in Ref. [1], the definition of dry-metal forming does not exclude the use of additives in the process, but rather focuses on the aspect that no additional cleaning or drying is needed in the subsequent processing step. Clearly, dry metal forming processes are challenging as the absence of lubricants typically results in an increased interaction at the interface between the work piece and the forming tool. Within a priority programme sponsored by the German Research Foundation, various groups have teamed-up to address these challenges.

Semi-finished products such as steel coils usually feature some oil or other fluids on the surface prior to forming. Thus, one key issue in the present research effort was to establish a defined surface condition for the dry forming experiments. The different research groups that take part in the priority programme study different materials and a wide range of production processes. A case in point are the extremely clean surfaces that are required for deposition of low friction, wear-resistant coatings on tools needed for dry metal forming. On the other hand, economic demands call for less sophisticated cleaning routines in the case of mass-produced work pieces. Interestingly, the work piece and forming tool can also represent different cases as regards the effect of residual lubricants present on the

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surface. When a coating is to be deposited on a tool surface by physical vapour deposition any contaminants will significantly degrade the coating's performance. By contrast, insufficient cleaning of the work piece might provide for lubrication, and thus, ease processing. The present paper reports on experiments that were designed to cover various surface conditions relevant for dry metal forming.

2 Experimental Details

Zinc coated DC04 sheet metal was used as the substrate in the present study. The material was shipped by the manufacturer with approx. 1 g/m^2 oil on the surface. In order to provide for a very clean initial reference condition, all specimens were cleaned as detailed in Fig. 1. In addition to the residues of hydrocarbons from fats and oils, oxides are expected on the surface of the sheet metal. Thus, an argon/oxygen-plasma (12 sccm Ar and 12 sccm O_2 at 0.2 mbar for 15 min) was used as the final step in initial cleaning (Fig. 1). This approach was used as high-energy UV radiation splits the macromolecules and oxygen radicals, ions and hydrogen radicals occupy free chain ends and finally form H_2O and CO_2. The degradation products of the hydrocarbons are gaseous and can be extracted by the low pressure environment. In addition, oxide layers adhering to the substrate are removed preferentially by the argon ions in the plasma. Due to the high kinetic energy, an additional microetching/cleaning is achieved.

Next, this surface (condition "A") was characterized using X-ray photoelectron spectroscopy (XPS). For the actual analysis the samples were exposed to an ultra-high vacuum (10^{-10} mbar) in an Axis Ultra XPS from Kratos Analytical Ltd. and the energies of the photoelectrons and Auger electrons emitted upon excitation by X-rays were determined. It should be noted that XPS probes only the composition of the near-surface layer (10 – 15 nm).

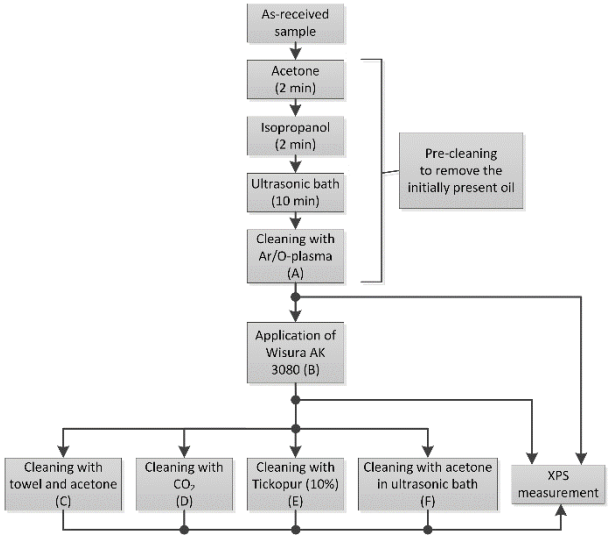


Fig. 1: Flow chart illustration the procedure employed to assess the effectiveness of different cleaning approaches

In order to assess the efficiency of various cleaning processes that might be used in future dry metal process chains, the plasma-etched references surfaces where then re-lubricated with Wisura AK 3080 (a commonly used lubricant) to provide for a constant lubricant content on the surfaces of 1 g/m^2 (condition "B" in Fig. 1). As shown in Fig. 1, four different cleaning procedures were then employed and the samples surfaces were finally analysed by XPS again. Specifically, the cleaning procedures included:

(i) Simple wiping with a white cotton cloth and acetone. This process was repeated until the cloth appeared stainless by visual inspection (condition "C" in Fig. 1).

(ii) A CO_2-based process, where the samples were mounted above four laser-drilled micro holes (diameter at the outlet: 440 µm). The nozzles had the contour of a diffuser to form as much CO_2 snow as possible. For cleaning, the CO_2 feed valve was kept open for 20 s. (condition "D").

(iii) Simple wiping with a white cotton cloth saturated with a Tickopur solution (10% Tickopur R33 in deionised water). Tickopur R33 (Dr. H. Stamm GmbH, Berlin) is an alkaline universal cleaner, which has been developed for cleaning and degreasing metals (condition "E").

(iv) Degreasing in an ultrasonic bath filled with acetone for 1 min. The sample was completely covered with acetone to avoid contact with the ambient air (condition "F").

Finally, the differently cleaned samples were characterized once more using XPS.

In addition, the surfaces were also characterised using a commercially available oil film gauge (NG1 from Infralytic GmbH), which allows for a contact-free and non-destructive measurement. This system employs infrared spectroscopy to measure the oil film thickness based on light absorption behaviour using the Beer-Lambert law [2, 3]. As the intensity of signals depends on both the oil film and the surface characteristics [2] the systems internal calibration for hot-galvanized steels was used. This, however, could not be employed to obtain absolute values for near-oil free surfaces. Thus, a microbalance was used to establish an extended calibration curve based on the mass of different amounts of applied lubricant.

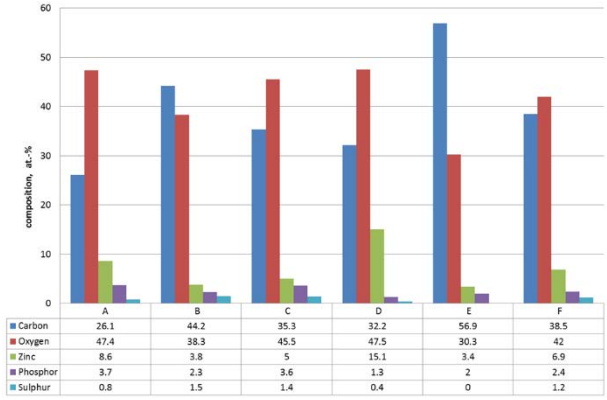
Wetting experiments were also employed to characterize the samples as wettability changes when residual lubricants, cleaning compounds or other contaminations are present on the surfaces after cleaning. In these experiments a defined drop of distilled water was applied to the surfaces and the contact angle was determined optically.

3 Results

3.1 Plasma-etched reference condition

As summarized in Fig. 2, in the reference condition, there were clear peaks from the coating on the substrate (Zn and P). The high oxygen content indicates that the top layer is in an oxidized condition. Interestingly, there is also a substantial amount of carbon demonstrating

that the plasma-etching could not fully remove the initially present contaminants. It should be noted XPS is a very surface sensitive technique that only probes the topmost layer. Obviously, on the re-lubricated surface (condition "B"), the carbon content is increased. Thus, the apparent content of the elements present in the coating gets lower as the contribution of the coating to the overall probed volume is curtailed. This effect is best seen if the nominal Zn-compositions are compared for condition "A" and "B".



	A	B	C	D	E	F
Carbon	26.1	44.2	35.3	32.2	56.9	38.5
Oxygen	47.4	38.3	45.5	47.5	30.3	42
Zinc	8.6	3.8	5	15.1	3.4	6.9
Phosphor	3.7	2.3	3.6	1.3	2	2.4
Sulphur	0.8	1.5	1.4	0.4	0	1.2

Fig. 2: Chemical composition of residual surface contamination present on the differently cleaned surfaces as determined by XPS analysis; see main text for details

In the present context it is also important to note that a substantial amount of surface layer may evaporate under the high-vacuum conditions ($\approx 10^{-10}$ mbar) needed for XPS analysis. In fact, the typical amount of 1g/m^2 of oil applied to a steel surface corresponds to a layer thickness of about 1000 nm. Given the fact that XPS probes only about 10 to 15 nm, the signal from the substrate should be completely absent in the spectra obtained from re-lubricated condition "B". Still, the signal from Zn was clearly present (Fig. 2), albeit at a lower level than after plasma cleaning (condition "A", Fig. 2). This indicates that most of the lubricant evaporates upon exposure to the high vacuum.

The fact that XPS probes only the surface layer, makes the technique also quite sensitive to local variations in chemical composition on the surface. This partly explains the obvious variability in carbon and oxygen content in the data shown in Fig. 2. Thus, in the present context the effectiveness of the different cleaning approaches is essentially assessed based on the apparent Zn-content, which is an approximate measure of contamination film thickness. Based on apparent Zn-content, it becomes obvious that neither of the towel-based approaches (samples "C" and "E") yielded very good cleaning results (low Zn-content plus high carbon content). By contrast, ultrasonic cleaning in acetone (sample "F") provided for a substantially higher Zn-content along with a high C-content in the signal. This indicates that only very thin layer of the lubricant has remained on the surface. Obviously, a fairly good cleaning result can be obtained by this rather simple approach.

Interestingly, the best cleaning results were achieved by the CO_2-based process (sample "D"). In fact, the apparent Zn-content is even higher than the one obtained for the plasma-etched reference condition "A", which could not remove all of the residues from the lubricant. Apparently, the CO_2 features very good solubility for the oil-based contaminations combined with some material removal from the surface caused by the mechanical impact.

3.2 Infrared Spectroscopy

The infrared-based oil film gauge is substantially different from XPS as it was designed to measure films with a thickness exceeding about 100 nm. Also the area probed is fairly large ($\approx$ 35 mm^2). Thus, one could expect that the data are substantially different. Interestingly, the overall trends were quite similar. The oil film gauge (with extended calibration curve on gravimetric measurements) demonstrated that the cleaning with cotton and acetone was not very efficient. For instance, the oil film thickness measurement indicated that about 10% of the initially applied lubricant was still present on the sheet for cleaning condition "C". Similarly, the ultrasonic cleaning turned out to be very efficient. In fact, within experimental scatter the surfaces were nominally oil-free in all other cases based on the oil film gauge data.

3.3 Wetting Experiments

For the wetting experiments, the samples were prepared as detailed in Fig. 1 and the contact angle, θ_1, was determined. In addition, a second set of samples was cleaned in an identical fashion but then also probed by XPS before the contact angle, θ_2, was evaluated. As summarized in Tab. 1, the contact angle θ_1 does vary substantially with the cleaning procedure. Moreover, the contact angle θ_2, i.e. the one obtained on the cleaned surface after an additional XPS analysis, can be higher or lower than θ_1 for different initial conditions. This change in contact angle following the XPS can be attributed to evaporation of residues on the surface in the high vacuum needed for the XPS measurements. This effect is most obvious for condition "B".

Tab. 1: Contact angle following different cleaning procedures; standard deviation was always less than 5° for 10 measurements

Surface condition / marked in Fig. 1 as	Θ_1, ° prior to XPS	Θ_2, ° after XPS
re-oiled / "B"	83	53
towel with acetone / "C"	81	54
CO_2 / "D"	60	75
10% Tickopur / "E"	13	64
acetone in ultrasonic bath / "F"	56	50

4 Discussion

At first glance, the overall trend obtained from the spectroscopic methods and the wetting experiments seem not be consistent. For instance, both of the spectroscopic methods have indicated that the towel-based approaches have resulted in inferior cleaning quality. By contrast, the wetting experiments show a very low contact angle of 13° after cleaning with Tickopur, which seems to indicate a good cleaning effect. Based on the spectroscopic analysis (Fig. 2) it is, however, clear that a substantial amount of residue is present after cleaning with Tickopur. Thus, the data summarized in Tab. 1 can be interpreted as follows: Both of the towel-based approach (condition "C" and "E") leave some residue on the surface. In case of the cleaning with acetone ("C"), the residue is quite hydrophobic, and thus, a large contact angle θ_1 results.

By contrast, the surface active agents from Tickopur ("E") render the surface hydrophilic. This explains the differences in contact angle θ_1 in the wetting experiments between the two conditions, and the substantial change to θ_2 as the residues get evaporated upon the XPS analysis, cf. Tab. 1. The surface active reagents (tensides), which are essentially composed of aliphatic hydrocarbon chains that remain on the surface, also explain the high carbon to oxygen ratio observed in the XPS data obtained from the surface cleaned with Tickopur (Fig. 2, condition "E"). The spectroscopic methods have indicated that both the CO_2 (condition "D") and cleaning with acetone in an ultrasonic bath (condition "F") have provided for good cleaning results. Again, the wetting experiments seem not to reflect the good cleaning as the contact angle θ_1 is around 55 to 60 ° in these cases. However, the fact that θ_1 is quite similar to θ_2 indicates that no substantial changes in surface properties have occurred. This indicates that evaporation was minimum during the XPS measurements, which hints at a very clean initial surface.

From the analysis of the data obtained by the different analytical techniques it becomes clear that the wetting experiments are not straightforward to interpret. Specifically, a low contact angle (condition "E" in Tab. 1) does not directly demonstrate wetting of a clean surface, and good cleaning might result only in intermediate contact angles (conditions "D" and "F" in Tab. 1). Still, wetting experiments can be employed as an easy to implement method to track changes occurring in cleaning processes as the contact angle is quite sensitive to changes in surface condition (Tab. 1).

Similarly, the XPS analysis has drawbacks and in the present case the data are clearly biased by evaporation of residues on the surface upon exposure to the high-vacuum environment. Still, the signal from the substrate could be used to assess the effectiveness of the different cleaning approaches employed. Specifically, the cleaning with CO_2 was demonstrated to be very effective (Fig. 2). It is well known that supercritical CO_2 has good solubility for lubricants [4]. Interestingly, the CO_2-based approach appeared to be even superior to plasma cleaning based on the magnitude from the signal of the substrate in the XPS spectra, cf. Fig. 2. This is consistent with data reported by Dong et al., which indicate that there is a fundamental limitation to plasma-based surface cleaning procedures on metal surfaces [5]. It should be noted, however, that the effectiveness of CO_2-based cleaning does depends substantially on the actual process parameters employed [6].

The commercially available IR-based oil film gauges are not designed for the low film thicknesses of interest in the present study. This limitation can, however, be overcome using a special calibration routine as addressed in section 3.2. As it appeared that this approach might be best suited for characterization of the surfaces in the context of dry metal forming, part of the experiments were repeated with two different aluminium alloy substrates (AA5182 and AA6014). The data are not shown here as the overall trends were quite similar, i.e. towel-based cleaning processes were inferior to the other methods, but residual film thickness did not exceed about 100 nm in all cases.

A still better cleaning result can be expected if hydrophobic and hydrophilic solutions are applied in an alternating fashion, such as used in the present study prior to plasma cleaning, cf. Fig. 1. In the context of dry metal forming it should be noted, however, that all the cleaning approaches employed left only a small amount of residue. Even with the inferior cleaning approaches the film thickness present on the surface did not exceed about 100 nm. Thus, it can be expected that this layer will not contribute significantly to typical forming processes such that metal-to-metal contacts will dominate after a few forming steps or cycles. In fact, the results obtained by the different groups working in the priority programme all indicate that friction and wear conditions in the different dry forming processes studied can be varied widely by appropriate surface modifications, e.g. [7, 8]. Thus, for the workpiece, a residual film thickness below 100 nm appears sufficient to mimic true dry-forming conditions in most cases, whereas other processes such as coating of the dry-forming tool will typically call for extremely clean surface that require multiple cleaning steps.

5 Conclusions

The residues on surfaces of workpieces used for dry-metal forming were analysed and the effectiveness of different cleaning approaches were evaluated. The results of the present study can be summarized as follows:

- The best results were obtained using a CO_2-based approach, which combines the high solubility for oil residues with effective removal of contaminations by the mechanical impact.
- However, even simple approaches like cleaning with a towel and acetone left only a film of about 100 nm on the surface.
- Only the combination of the different analytical techniques employed (XPS, IR-

spectroscopy, wetting experiments) allowed for a comprehensive characterisation of the surface condition.
- For routine control of the cleanliness of surfaces, an IR-based oil film gauge with an extended custom calibration turned to be the best approach in terms of ease of interpretation and accuracy.

Acknowledgements

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