

Numerical Simulation of Galvanic Corrosion and High Temperature Corrosion During Hot Metal Stamping Process

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Abstract

The article presents a comparative analysis of the simulation results with the results of experiments on corrosion processes occurring at elevated temperatures (high-temperature corrosion) and in conditions of combined corrosion (chemical, in water, and electrochemical, galvanic steam). Good relation of the results at the level of the expected products of chemical interaction is obtained.

Keywords: corrosion; numerical simulation; high temperature corrosion; oxide scaling; Comsol Multiphysics; galvanic corrosion; hot metal stamping.

1. Introduction

Corrosion processes are one of the main problems of machine failure and require a responsible approach to finding solutions to prevent them. Corrosion processes are subdivided according to the mechanism of occurrence into chemical, electrochemical, radiation, biological, and others [1]. According to the type of aggressive environment, corrosion can be gaseous, atmospheric, electrolytic. Also, according to the nature of the change in the surface of the metal with a change in its physical and mechanical properties, corrosion can be uniform and uneven, spots, ulcers, dots, subsurface, intergranular, structurally selective. Corrosion modeling is a rather complicated process, since it is necessary to accurately set the parameters of the ongoing physical process.

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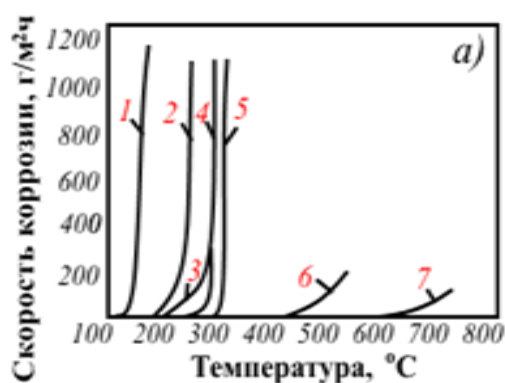
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In addition, the object may be subjected to additional effects, such as heat, friction, stress, cavitation, and other means. In this paper, atmospheric corrosion with thermal effects (high-temperature corrosion) was considered, as well as combined chemical and electrochemical corrosion with oxygen depolarization. It is known that during high-temperature corrosion, three oxide films (oxides) are formed, and the oxide with the lowest oxygen content is in contact with the base metal. Oxides include: wuestite (FeO), magnetite (Fe_3O_4) and hematite (Fe_2O_3). Natural experiments were carried out to verify the simulation results.

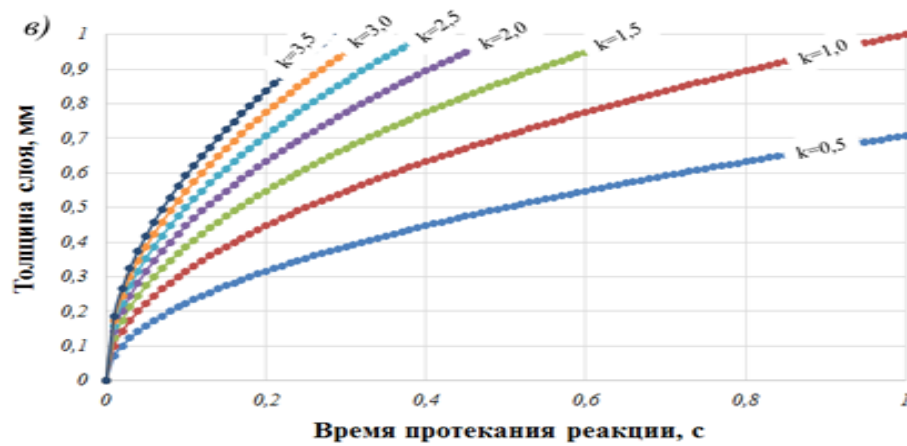
Since corrosion is a diffusion process, the temperature and humidity of the air have a very strong influence on it. Figures 1a and 1b show experimental graphs of oxide layer growth on the surface of different metals, and figure 1c shows the theoretical definition of oxide film thickness growth in accordance with equation 1 [1]. Figure 2a shows the design scheme for the occurrence of high-temperature corrosion (task No. 1), and Figure 2b shows the design scheme for the occurrence of combined corrosion (task No. 2). Standard values of electrode potentials are given in Table 2[2].



a) corrosion rate in dry chlorine atmosphere: 1 – Al; 2 - gray cast iron; 3 - Cu; 4 - carbon steel; 5 – Fe-Armco; 6 - 10X18H10T; 7 – Ni [3].



b) influence of relative humidity and atmospheric pollution on corrosion: 1 – clean air; 2 – air with 0.1% SO_2 ; 3 – air with 0.01% SO_2 and charcoal dust [4].



c) theoretical graphs of scale growth

Figure1: Graphs of the growth of oxide films under different conditions.

$$h^2 = k\tau, \quad (1)$$

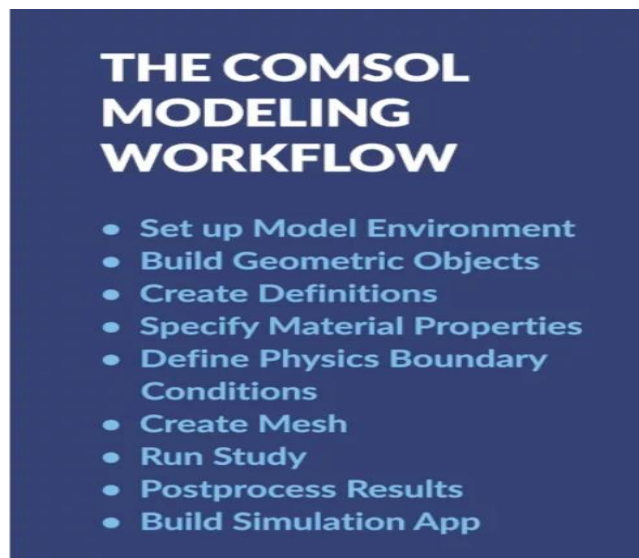


Figure 8

where h is the thickness of the oxide film; k is the diffusion rate constant; τ - oxidation time.

2. Materials and Methods

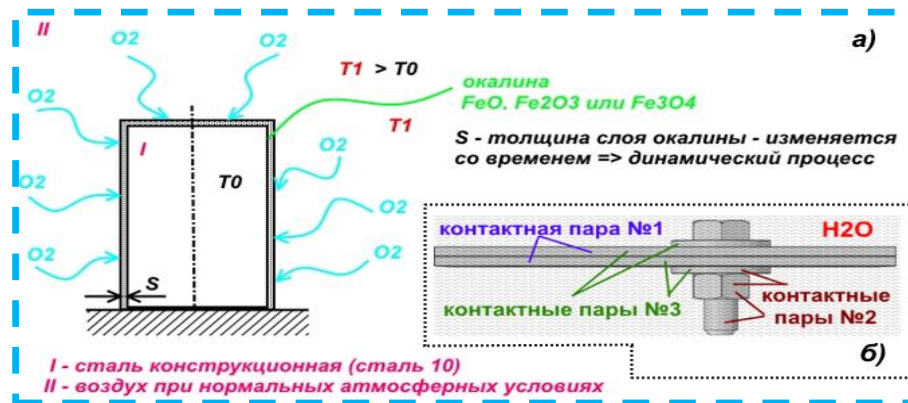


Figure 2: Schematic representation of the conditions of the problem.

Studies on high-temperature corrosion were carried out on cylindrical samples of steel 10 with dimensions $H=70$ mm and $\varnothing 100$ mm that were heated to a temperature of 900°C in an electric furnace with a chamber not isolated from the atmosphere. After that, the samples were removed from the furnace and cooled in air.

After complete cooling, scale was removed from the surface of the sample using metal brushes and the mass and thickness of the oxide were determined (Table 1).

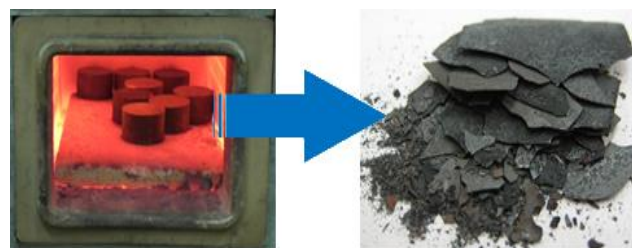


Figure 3: Heating samples in an electric furnace (left) and scale (after cleaning the sample, right).

Table 1: Results for experiments on task No1.

Temperature of the sample, $^\circ\text{C}$	Environment temp $^\circ\text{C}$	Sample Mass, g	Oxide scale Mass, g	Oxide scale thickness, mm
900	20	411	3.10	0.87
900	20	403	2.85	0.35
900	20	398	2.98	0.46
900	20	397	2.90	0.78
900	20	399	2.91	0.83
900	20	412	3.25	1.20
900	20	410	3.00	0.90

2.1 Oxide formation

In situations with oxygen, the majority of metals are thermodynamically unstable and will hence react to

generate oxides. At high temperatures, such as those seen in hot metal stamping, the reaction rate may become problematic due to material deterioration because it increases quickly with temperature. Typically, the interaction of a metal with oxygen to create an oxide represents an oxidation reaction. You can write down the chemical reaction between a metal M and oxygen gas O₂ to create the oxide MO as follows:



As shown in Figure below, the oxidation process can be broken down into three parts. In the first step (a), oxygen is taken in, dissociated on the clean metal surface, and then formed into O²⁻ by a charge transfer. Individual oxide nuclei arise in step 2 (b). On the surface, the nuclei expand laterally until a continuous film is produced. The reaction can only continue through solid state diffusion of the reactants through the film in the third step (c), where the surface oxide isolates the metal from the gas. Temperature affects the diffusion rate through the oxide, which is almost zero at ambient temperature. But when the temperature rises, the diffusion rate increases and the oxide begins to build.

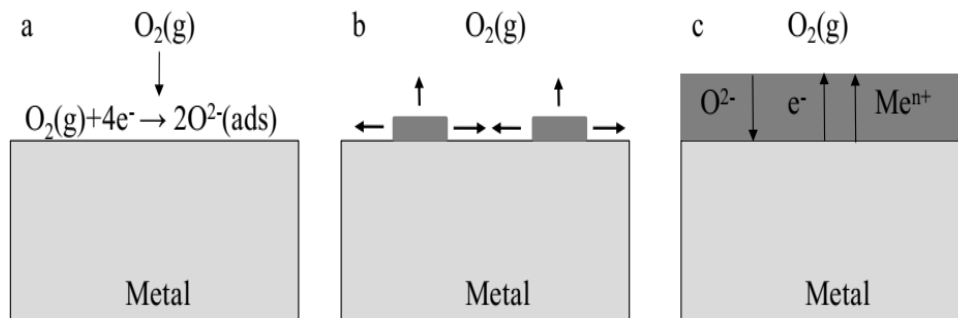


Figure 4: The initial formation of an oxide scale by adsorption of oxygen, oxide nucleation and growth to form a continuous oxide scale (stages a–c).

A metal sample steadily gains weight while oxidizing. Equation 2's reaction, which occurs as the metal oxide forms, is the cause of this weight growth. Measuring the weight change of the metal as it reacts with the gas is a standard approach to monitor and investigate the oxidation rate. Information about the reaction mechanism and the rate-limiting stage of the entire reaction is provided by this type of study. There are three types of rate equations that are frequently used: logarithmic, parabolic, and linear behavior.

The illustration below. It's crucial to keep in mind that the principles are developed from highly idealized models that frequently only fully capture the behavior of oxidation.

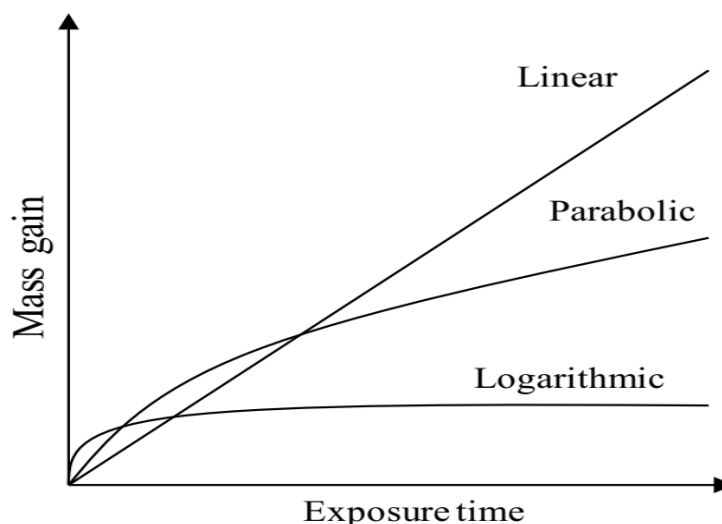


Figure 5: Mass gain versus exposure time for linear, parabolic and logarithmic growth.

2.2 Parabolic kinetics

When using parabolic kinetics, the initial rate of oxide formation is rapid, and it slows down over time. At high temperatures, the majority of metals and alloys exhibit a parabolic rate [14]. Mathematically, the parabolic kinetics model is written as:

$$X^2 = K_p t + A \quad (3)$$

where t is the passage of time, A is integration, and x is the thickness of the oxide. Wagner claims that the lattice passage of reaction atoms, ions, or electrons through the oxide layer is the rate-regulating step for oxide formation on a metal; as the oxide layer thickens, the corrosion rate declines. Wagner produced an expression for k_p in his hypothesis using the oxide's electrical and ionic conductivity.

Wagner's model, however, only takes into account the rate-determining step of atom, ion, and electron transport on the lattice. The model is therefore predicated on the following suppositions: the oxide layer is compact, single-phased, and well adherent; the oxide exhibits only minor departures from stoichiometry; oxygen solubility in the metal may be disregarded; diffusion of ions and electrons must be the rate-determining step; and the thermodynamic equilibrium is preserved at the two interfaces as well as in the oxide.

For task No. 2, samples were prepared, consisting of several contact pairs, which were placed in open containers with tap water for more than 48 hours. After that, the places of chemical activity were determined by visual inspection.

Table 2: The value of the standard electrode potentials of metals (in aqueous solutions at 25°C).

<i>Metal</i>	<i>Electrode Process</i>	<i>Standard electrode Potential, V</i>	<i>Contactpairs, (KP1,KP2,KP3)</i>
Aluminum (Al)	$\text{Al} \rightarrow \text{Al}^{3+}$	-1,660	KP1: Cu+Fe(galvanized) KP2: (Cu-Zn) + Fe KP3: (Cu-Zn) + Fe
Steel (Fe)	$\text{Fe} \rightarrow \text{Fe}^{2+}$	-0.430	
Copper (Cu)	$\text{Cu} \rightarrow \text{Cu}^{2+}$	+0.337	
Steel (stainless steel)	n/a	n/a	
Zinc (Zn)	$\text{Zn} \rightarrow \text{Zn}^{2+}$	-0.76	
Brass (Cu-Zn)	n/a	-0.35	

The simulation was carried out in the Comsol v.5.3 program, based on the finite element method, in the electrochemistry and heat-mass transfer modules. Problem No. 1 was modelled as axisymmetric. The following boundary conditions were assigned: heat exchange at all ends (option 1); on the upper end and side surfaces - heat exchange with the environment, on the lower face - an insulating plate (option 2). Problem No. 2 was modelled under conditions of 100% humidity with heat exchange over all faces.

3. Results

3.1 Task No1

The simulation results of problem No. 1 are presented in Table 2. The range of Scale growth corresponds to the theoretical calculation graphs, according to which scale growth occurs in the first two minutes. Starting from 200 seconds, the gross thickness practically does not change. The results of the simulation showed that high temperature corrosion is generally faster when the metal under consideration is not placed on any insulation plate after being heated. This is because when a metal is heated, it can react with the surrounding environment, such as oxygen, water vapour, or other gases, to form corrosion products. If the metal is not insulated, it will be exposed to a greater amount of these reactive species, which can accelerate the corrosion process. On the other hand, if the metal is placed on an insulation plate, it will be shielded from some of these reactive species, which can slow down the corrosion process. We will consider the results where there was no insulation plate since they correspond to the experimental setup during the conduction of experiments.

Scale growth in the direction from the axis to the radius has a minimum radius of 3.2mm and a maximum of 4.9mm (Graphs 1a, b).

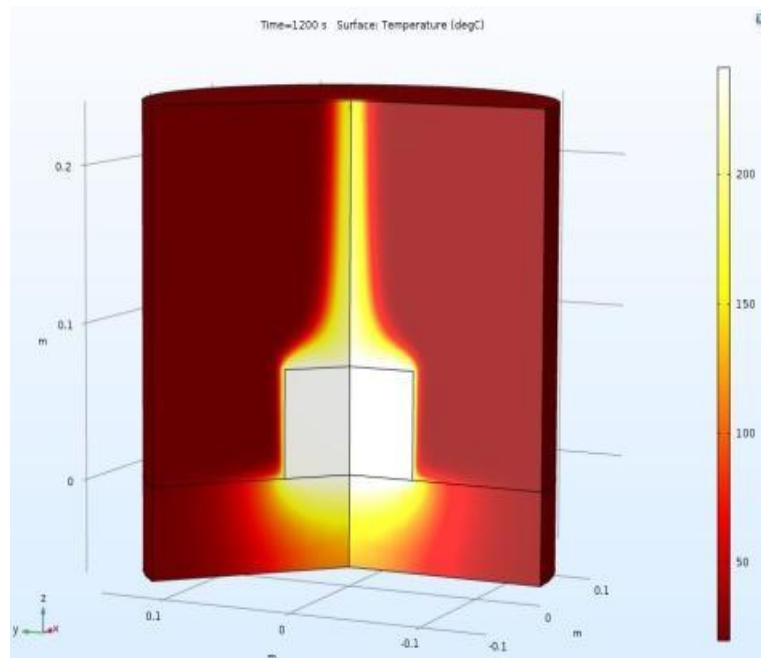
Scale growth in the direction along the axis has a minimum value of 0.7mm and a maximum of 3.5mm.

Scale growth on the upper edge and at the central part of the upper end range from 0.3mm to 8mm.

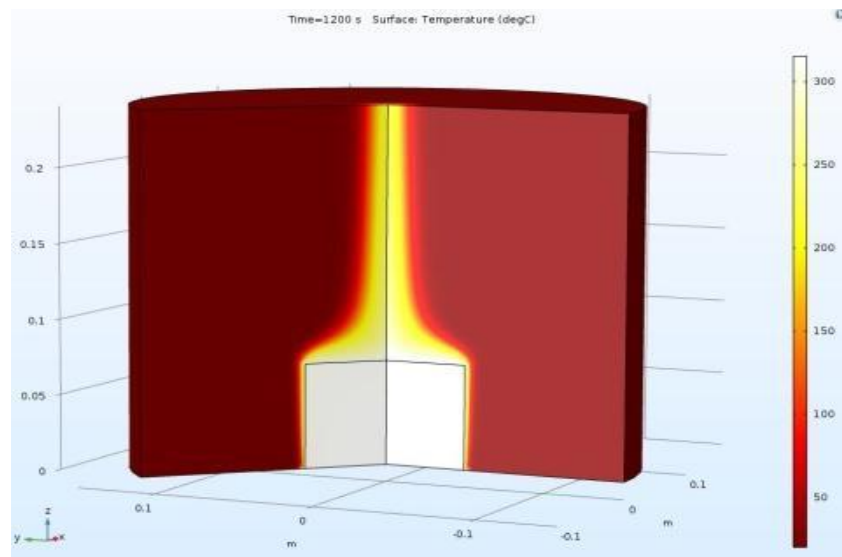
The results of the experiments fall within the range of the simulation results even though in simulations the

maximum value for the oxide scale width was much higher as the program continues to iterate the reaction at the same temperature where as in real life the reaction takes place within a certain period of time as the metal cools down.

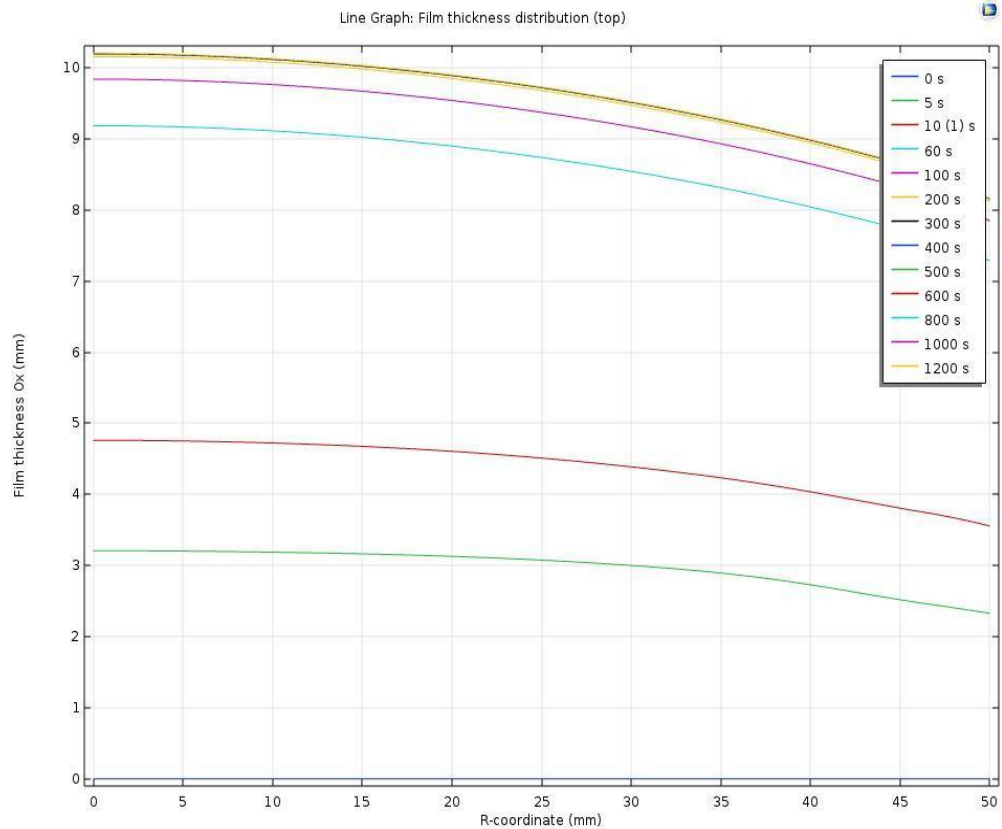
Option 1: without insulating plate



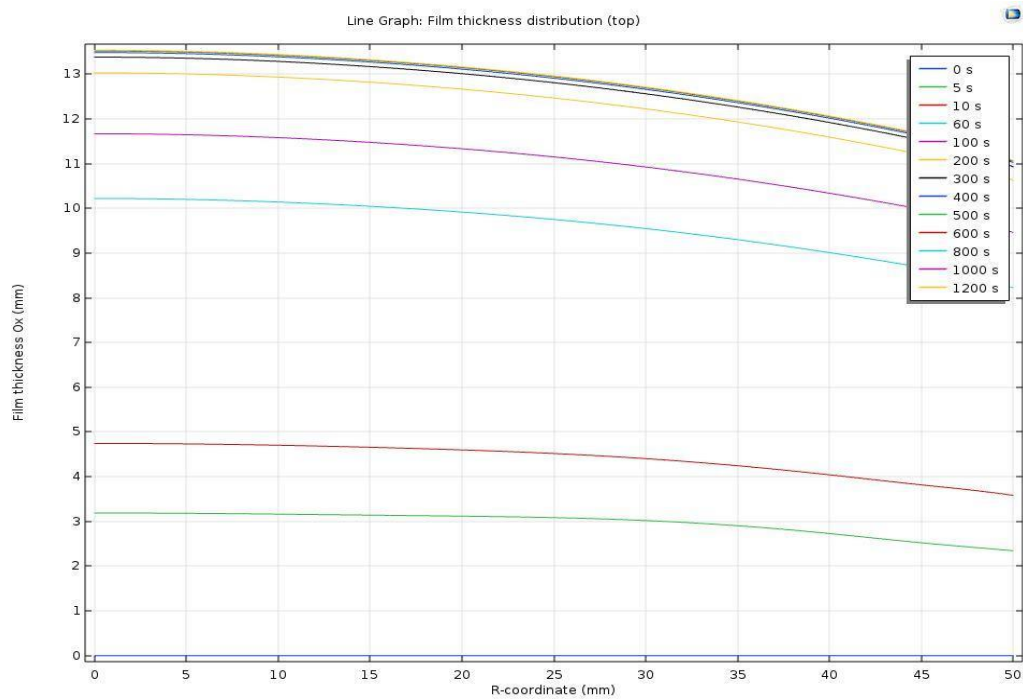
1a) boundary conditions.



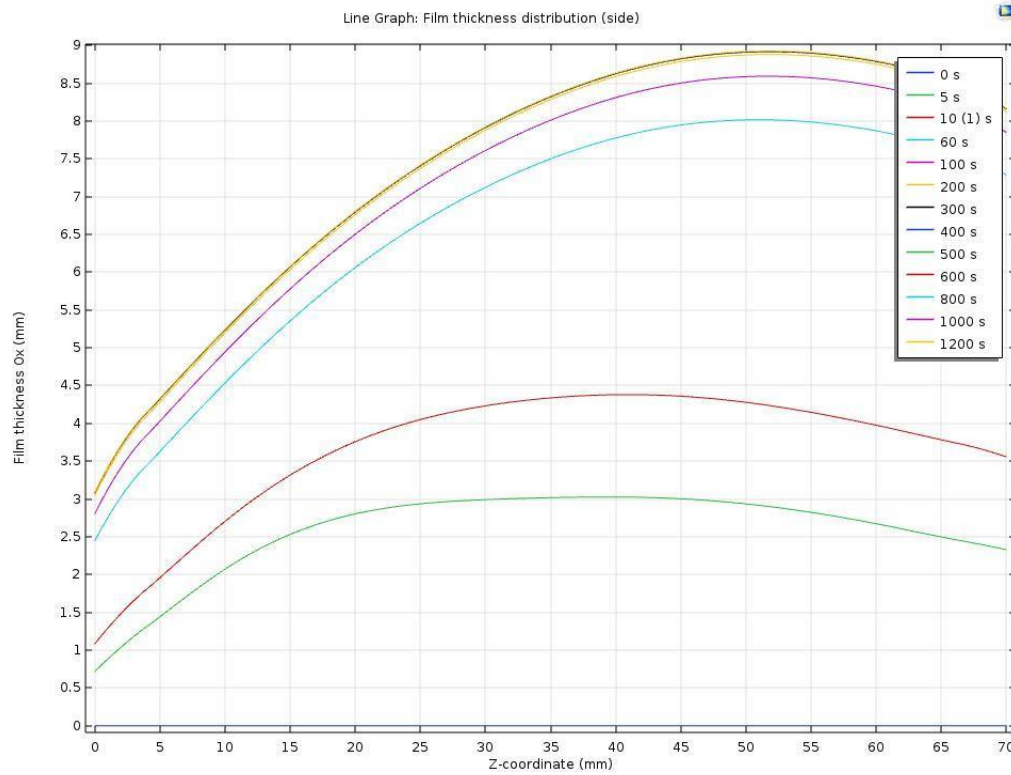
1b) Option 2: with insulating plate.



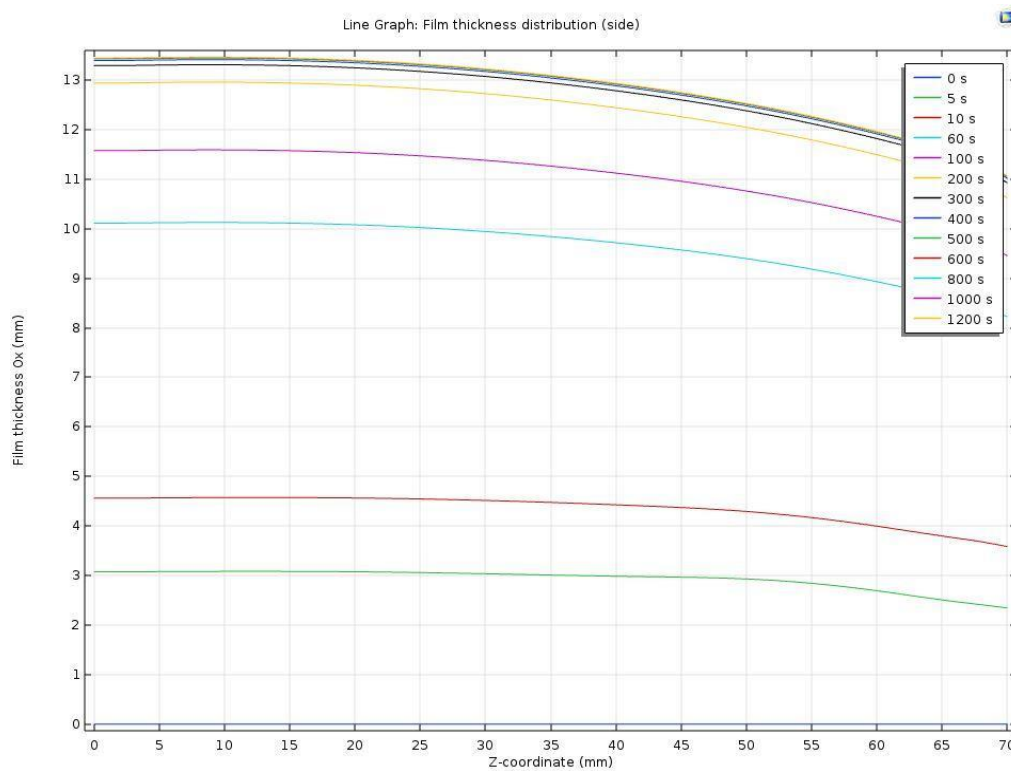
2a) scale growth in the direction from the axis to the radius without insulating plate.



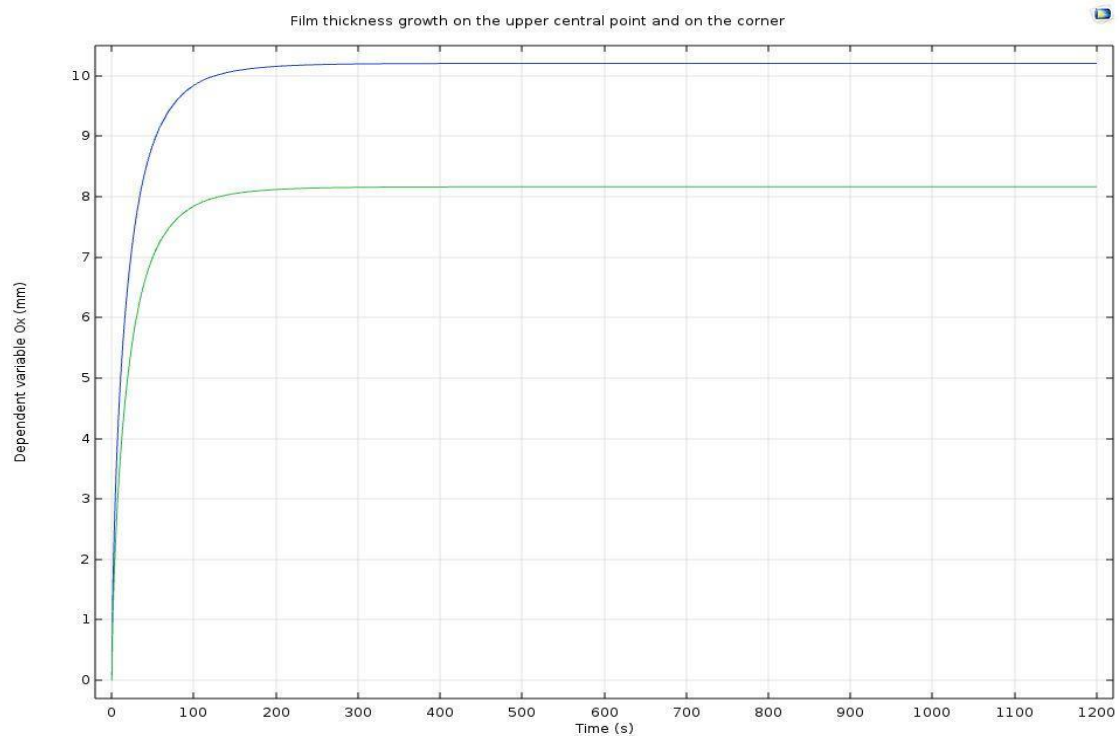
2b) scale growth in the direction from the axis to the radius (with insulating plate).



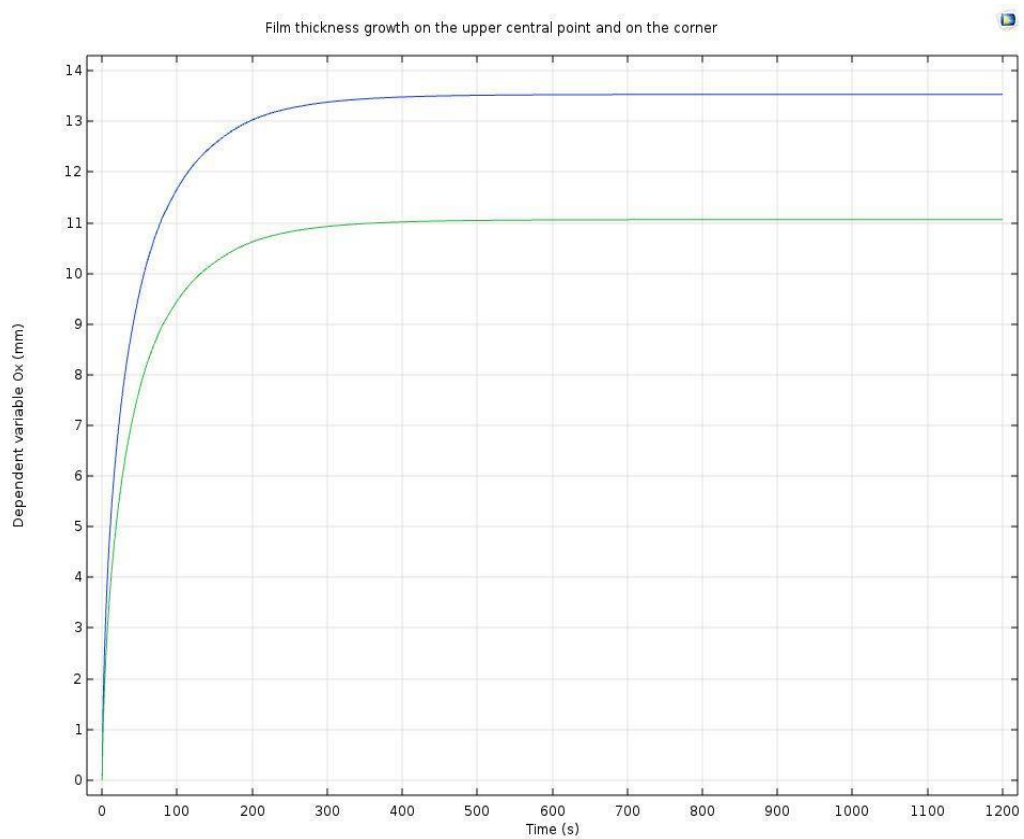
3a) scale growth in the direction along the axis (without insulating plate).



3b) scale growth in the direction along the axis (with insulating plate).



4a) growth of scale on the upper edge and at the central point of the upper end (without insulating plate).



4b) growth of scale on the upper edge and at the central point of the upper end (with insulating plate).

Figure 8: Simulation results for problem No1.

3.2 Task No 2

The simulation result of problem No. 2 is shown in Figure 6. It is known that CP1 forms a galvanic pair and is dangerous for iron, since a stable cathode state is formed. In view of the shortness of time, the largest reaction product was observed not for contact pairs (electrochemical corrosion), but for individual elements (chemical corrosion) due to high humidity. It can be seen that at the point of contact of CP1, the reaction actively proceeds with the formation of a white deposit. In this case, copper carbonate (CuCO_3) is formed, and the very surface of the copper plate is covered with a thin oxide - copper hydroxide $\text{Cu}(\text{OH})_2$ (Figure 6a). Iron coated with zinc does not participate in this reaction, since Zn ("sacrificial coating") protects the substrate from corrosion. A black coating forms on the brass nut - a thin layer of patina (Figure 6c). The simulation results show that over time (more than 48 hours), the results of electrochemical corrosion will also be visible at the junction of the plates (Figure 6b) and at CP2 and CP3 (Figure 6d).

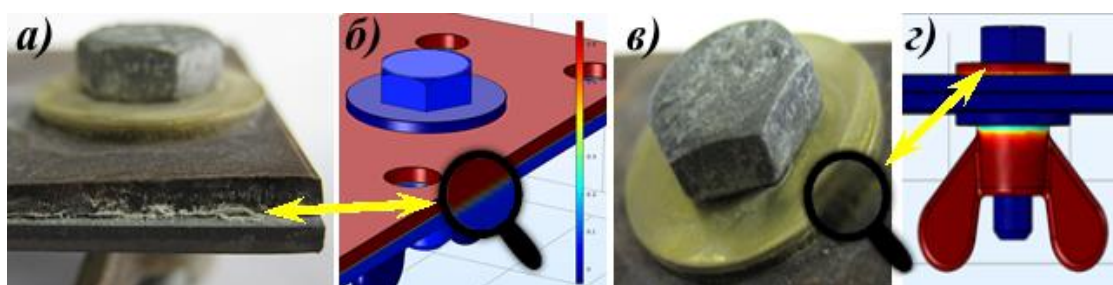


Figure 6: Simulation results of problem No. 2 (a - CP1, white coating (exp.); b - electrochemical reaction on the contact CP1 (model); c - black coating on the side surface of the brass washer (exp.); d - electrochemical reaction on the contact CP3 (model).

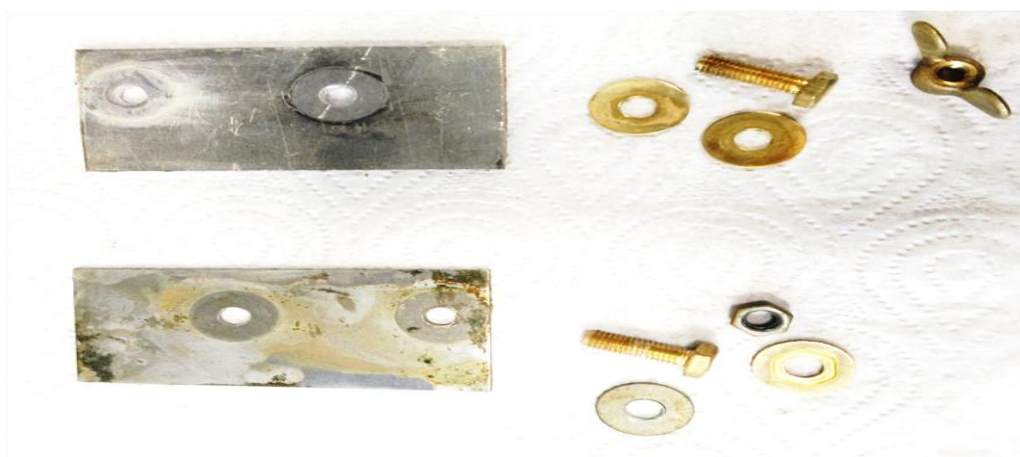


Figure 7: Exploded view of contact pairs.

The obtained results of verification (comparison) of experimental and numerical studies match. It is planned to conduct refined computer simulations with the determination of the mass and chemical composition of the corroded substance, as well as with the results of longer experiments.

4. Constraints/limitations of the study

While numerical simulation is a powerful tool for predicting and mitigating galvanic corrosion and high temperature corrosion during hot metal stamping, there are several constraints and limitations that should be considered. Some of these include:

Model accuracy: The accuracy of numerical simulation models depends on the quality and completeness of the input data, as well as the assumptions and simplifications made in the model. Inaccurate or incomplete data can lead to inaccurate or less accurate predictions, and simplifications can lead to oversimplification of the problem and inaccurate results.

Computational resources: Numerical simulation models can be computationally intensive and require significant computational resources, such as high-performance computing clusters or specialized software like in this case we made use of Comsol Multiphysics software which is not an open source software so we had to seek permission to be allowed full access for a limited period of time. This can limit the ability to perform simulations on a large scale and for a prolonged period of time.

Model validation: Numerical simulation models must be validated against experimental data to ensure their accuracy and reliability. In this case our constrain was that the program continues to iterate the reaction at the same temperature where as in real life the reaction takes place within a certain period of time as the metal cools down.

Material properties: The accuracy of numerical simulation models depends on the accuracy of the material properties used in the model, such as thermal conductivity, specific heat, and corrosion rates. However, these properties can vary depending on the specific material and the environment in which it is used, which can limit the accuracy of the model.

Model complexity: Numerical simulation models can become very complex, especially when multiple physical phenomena are involved, such as thermo-mechanical-electrochemical coupling. This can make it difficult to understand and interpret the results, and can limit the ability to optimize the process or design.

5. Conclusion

Numerical simulation has emerged as a powerful tool for predicting and mitigating galvanic corrosion and high temperature corrosion during hot metal stamping. Several studies have investigated the mechanisms and factors that influence corrosion during this process, and have identified important parameters such as contact pressure, temperature, electrolyte concentration, heating rate, and relative humidity. These findings can help to optimize the hot metal stamping process and improve the performance and lifespan of the stamped parts.

1) Comparison of experimental results, theoretical calculations and numerical simulations showed that with high-temperature, scale corrosion builds up quickly and after a certain time there is a saturation of the surface with oxygen.

- Saturation of surface with oxygen and absence of free.
- electrons and its thickness ceases to change.

2) Comparison of electrochemical and galvanic shows that a salt deposit is formed between the plates, and at the joint of the threaded joint rust is formed.

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7. Discussion

Hot metal stamping is a widely used manufacturing process in the automotive industry, which involves heating a metal sheet and then stamping it into a desired shape. However, this process can lead to galvanic corrosion and high temperature corrosion, which can cause structural damage and reduce the lifespan of the stamped parts. Numerical simulation has emerged as a powerful tool for predicting and mitigating these types of corrosion, and several studies have been conducted to investigate the mechanisms and factors that influence corrosion during hot metal stamping.

High Temperature Corrosion: High temperature corrosion occurs when a metal is exposed to high temperatures and reactive species, such as oxygen, water vapor, or other gases. In hot metal stamping, high temperature corrosion can occur when the metal sheet is heated to high temperatures, which can cause the formation of oxide scales and other corrosion products. Several studies have used numerical simulation to investigate the effects of high temperature corrosion during hot metal stamping. For example,[7] used a finite element model to simulate the high temperature corrosion of a steel sheet during hot stamping, and found that the corrosion rate was influenced by the heating rate, temperature, and oxygen concentration. Similarly, [8] used a thermo-mechanical

model to simulate the high temperature corrosion of a magnesium alloy during hot stamping, and found that the corrosion rate was influenced by the heating rate, temperature, and relative humidity.

Galvanic Corrosion:

Galvanic corrosion occurs when two different metals are in contact with each other in the presence of an electrolyte, such as saltwater or acidic solution. In hot metal stamping, galvanic corrosion can occur when dissimilar metals are in contact with each other, such as when a steel sheet is stamped onto an aluminum alloy. Several studies have used numerical simulation to investigate the effects of galvanic corrosion during hot metal stamping. For example, [9] used a finite element model to simulate the galvanic corrosion between a steel sheet and an aluminum alloy during hot stamping, and found that the corrosion rate was influenced by the contact pressure, temperature, and electrolyte concentration. Similarly, Zhang and colleagues (2020) used a coupled thermo-mechanical-electrochemical model to simulate the galvanic corrosion between a steel sheet and a magnesium alloy during hot stamping, and found that the corrosion rate was influenced by the contact area, temperature, and relative humidity.

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