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Localized acidity generation as a crux of microbially influenced corrosion

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Abstract

Microbially influenced corrosion (MIC) is of great industrial concern. Direct electron uptake from metal surfaces was shown to be an important MIC-process. Coupling of electron uptake from metal surfaces to sulphate-, nitrate-, nitrite- or CO₂-reduction is proton-mediated. Some sulphate-reducing bacteria and methanogens were shown to regulate pH of the environment, and we propose that they need this capability, particularly, to enable themselves to uptake electrons from metal surfaces. We also propose that corrosion-aggravating nitrate- and nitrite-reducing microorganisms are also likely capable of pH-regulation and that localized acidity generation by respiratory and methanogenic microorganisms is one of the key MIC-processes. Future experiments involving measurements of ion and gas concentrations at metal – biofilm interfaces and transcriptomics analyses can help verify these assumptions.

Common initiators and products of iron corrosion

Corrosion of iron (Fe⁰), i.e. its transformation/dissolution into Fe²⁺, can be coupled to the reduction of a number of oxidizing agents, such as O₂, H⁺, S⁺⁶ in SO₄²⁻, S⁰, N⁺³ in NO₂⁻, N⁺⁵ in NO₃⁻, or even C⁺⁴ in CO₂; ferrous iron can be further oxidized to Fe³⁺. Formation of insoluble ferrous and/or ferric compounds most often follows this process, for example, in the case of oxygen as an oxidizing agent, iron oxide(s) and/or hydroxide(s) are formed.

In the case of an oxidizing agent having high reduction potential, such as O₂, iron dissolution easily occurs purely electrochemically; thus, the mere exposure of an iron/steel surface to oxygen (i.e. either to air or water where it is dissolved) is a factor of corrosion. In the case of oxidizing agents having lower reduction potentials, the main or the only drivers of iron dissolution are often microorganisms.

Insoluble products of corrosion can have either harmful or beneficial effects, e.g. ferrous sulfide can initiate/facilitate pitting corrosion and/or lead to sulfide stress cracking (Eklund, 1974; Kane and Cayard, 1998); on the other hand, in some conditions, insoluble products of corrosion can form films protecting metal surfaces against further corrosion (Ma et al., 2000). Thus, microbiologically influenced corrosion inhibition (MICI) sometimes occurs (Kip and van Veen, 2015; Videla and Herrera, 2009; Zuo, 2007).

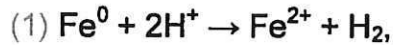
MIC types

MIC mechanisms were reviewed in recent years by a few authors (e.g. Enning and Garrelfs, 2014; Gu, 2012; Kip and van Veen, 2015; Videla and Herrera, 2005). Generally, MIC occurs in anoxic environments due to the activities of sessile cells in biofilms (Gu, 2012).

According to Gu (2012), there are at least two distinct types of anaerobic MIC. Type I MIC occurs due to the activities of respiratory or methanogenic microorganisms, which are capable of using metal electrons as a source of energy (Gu, 2012). Concepts of GUME (growth upon metallic electrons) and EMIC (electrical microbially influenced

corrosion) recently used in the literature (by Dronen et al., 2014 and by Enning and Garrelfs, 2014, respectively) refer to Type I MIC.

Type II MIC, according to Gu (2012), occurs due to the activities of fermentative acid producing bacteria (APB). Proton reduction can be chemically coupled to iron oxidation:

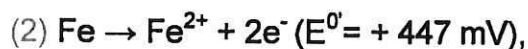


and APB can aggravate corrosion through acidification of the environment in the vicinity of a metal surface. In addition to corrosion acceleration through creating “demand for electrons” by protons, a low-pH environment was also shown to inhibit formation of passivating films (Olsson and Landolt, 2003). Undissociated organic acids, such as free acetic acid, may serve as a proton reservoir and/or be reduced directly (Gu, 2012).

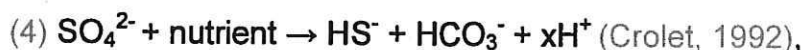
It is interesting that, in fact, some respiratory microorganisms are capable of lowering pH as well. Daumas et al. (1993) found such a capability, in particular, in the sulphate reducing bacterium (SRB) *Desulfovibrio fructosovorans*. It is not known, however, how widespread this capability is among respiratory bacteria and methanogenic archaea involved in MIC. If it is widespread among them, then a proton attack on a metal surface may be characteristic of not only Type II MIC, but of Type I MIC as well. Below, we will briefly review previously described mechanisms of the corrosive activities of SRB, nitrate reducing bacteria (NRB) and methanogens to try to predict whether the capability of lowering pH at metal – biofilm interfaces is common among some or all of these microorganisms.

Corrosive role of SRB

SRB have been best known as microorganisms that can aggravate iron corrosion (Enning and Garrelfs, 2014). MIC by SRB occurs due to their capability of coupling utilization of electrons from iron oxidation to sulfate reduction:

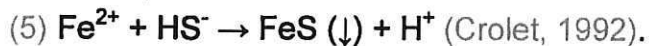


Provided that sulfate reduction is catalyzed by an SRB biofilm, the process consisting of these two reactions is thermodynamically favourable: a combined redox potential is positive: $447 - 217 = + 230 \text{ mV}$, i.e. combined Gibbs free energy is negative (Thauer et al., 2007). According to Gu (2014), sulfate reduction by SRB (e.g. *D. vulgaris*) does not cause a net change in scalar or vectorial protons, and the protons are present in the equation (3) just for balancing the half reaction stoichiometrically. However, findings reported long time ago by Daumas et al. (1993) make one think that sufficient local acidity is, in fact, necessary for the reaction (3). Daumas et al. (1993) showed that SRB were capable of regulating pH of the environment. Acidity generation mediated by SRB occurs, generally, as follows:



where x can, in principle, be either positive or negative, depending on the original pH of the environment and on the nature of the consumed nutrient (Daumas et al., 1993). Contrary to the conclusions by Gu (2014), in the experiments conducted by Daumas et al. (1993), "net acidity production" was observed at pH 7.2 and 8.5, and "net acidity consumption" by SRB was observed at pH 6. Obviously, SRB would strive for creating generally comfortable environment for themselves, and one can think that they needed the "net acidity production" exactly to make enough protons available for the reaction (3).

Solid-state iron sulfide precipitation, which is often linked to reactions (2) and (3), can contribute to maintaining low pH:



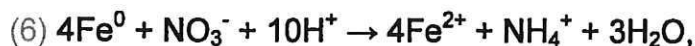
As mentioned above (and explained, e.g., by Eklund, 1974; Kane and Cayard, 1998; and Ma et al., 2000), the formation of iron sulfide can be either harmful or beneficial and, thus, should not always be considered a corrosion event.

Removal of hydrogen gas by hydrogenotrophic SRB is also not always a corrosion event, contrary to the cathodic depolarization theory (CDT; von Wolzogen Kühr and van der Vlugt, 1934). H_2 does not inhibit its own formation on iron (Cord-Ruwisch, 2000). However, provided that the assumption about "net acidity production" preceding reactions (2) and (3) is correct, stimulation of iron oxidation due to consumption of H_2 should be expected to occur when H_2 is the nutrient and x is positive in reaction (4).

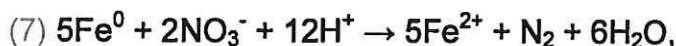
Corrosive role of NRB

Iron oxidation coupled to purely chemical or microbially mediated nitrate reduction (i.e. reduction of N^{+5} in NO_3^-) is a well-known phenomenon (Dronen et al., 2014; Huang et al., 1998; Lino et al., 2015; Till et al., 1998; Xu et al., 2013).

In the case of iron corrosion coupled to abiotic nitrate reduction, the reaction can proceed as follows:



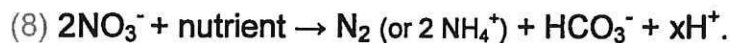
Formation of nitrogen gas as an end product of abiotic nitrate reduction is possible as well:



particularly, in unbuffered anoxic media (Huang et al., 1998; Lin et al., 2008). In the case of iron corrosion coupled to microbially mediated nitrate reduction, either ammonium or nitrogen gas, likewise, can be the products (reactions (6) and (7) respectively). Reaction (7) has a standard potential of +760 mV (Thauer et al., 2007). It is much higher than the combined redox potential of reactions (2) and (3), and this

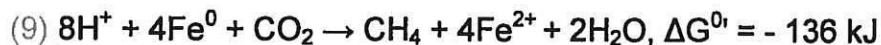
means that NRB-aggravated metal corrosion can potentially be more severe than SRB-aggravated corrosion (Gu, 2014).

Protons are the reactants in both reactions (6) and (7); chemical reduction of nitrite (which is often an intermediary product) is proton-dependent as well. It was shown that chemical reduction of nitrate and nitrite, indeed, depended on pH in both buffered and unbuffered solutions (Lin et al., 2008). When reactions (6) and (7) are microbially mediated, protons are still the reactants, similarly to the situation with sulfate reduction. It is logical to predict that, similarly to the case of microbial sulfate reduction (reactions 2, 3 and 4), microbial nitrate reduction coupled to the oxidation of limited organic nutrients leading to proton/acidity generation, would precede microbially mediated reactions (6) or (7) in the case of the initially neutral or basic pH at a metal – biofilm interface:



Corrosive role of methanogens

Daniels et al. (1987) found indications of the contribution of methanogens to the corrosion of iron-containing materials in anaerobic environments. Iron-dependent methane production involving the direct uptake of electrons from an iron surface and CO₂ reduction was later observed by Dinh et al. (2004):



A free energy change in reaction (9) is very similar to that in methanogenic H₂ oxidation:



Consistently with the fact that protons are among the reactants in reaction (9), Boopathy and Daniels (1991) found that pH optima for *Methanococcus deltae*, *Methanococcus thermolithotrophicus* and *Methanosarcina barkeri* were lower when the H₂ availability was limited and Fe⁰ was provided (from 5.4 to 6.5), compared to their pH optima in the case of abundantly available H₂ and CO₂ (from 6.2 to 7.0). It appears to be likely that in the case of having H₂ in abundance, these archaea may preferentially produce methane through reaction (10), although in the case of limited hydrogen availability, they may either generate acidity on their own (using hydrogenases, with which hydrogenotrophic archaea are well-equipped; Thauer et al., 2010) or use protons produced by other microorganisms at a metal – biofilm interface to proceed with reaction (9).

The roles of nutrient limitation and acidity generation in MIC

To explain Type I MIC, i.e. that occurring due to the activities of respiratory or methanogenic “X-reducing” prokaryotes (“XRP”; X standing for an oxidant other than oxygen, such as sulfate, nitrate, nitrite, sulfur or CO₂), Xu and Gu (2011) suggested the Biocatalytic Cathodic X Reduction (BCXR) theory. According to this theory,

microorganisms can begin using Fe^0 as the electron donor, particularly, when there is local shortage of organic electron donors, which can happen at the metal-biofilm interface due to diffusion limitations (Stewart, 2003).

In the situation described in Fig. 1A, if a medium is nutrient-rich, then a thick and heterogeneous biofilm (heterogeneous in terms of its physical structure and chemical and microbial community compositions; Flemming and Wingender, 2010) may be formed (Fig. 1B). In such a biofilm, indeed, a shortage of organic electron donors may be experienced by some microorganisms located at the metal-biofilm interface, leading to the need to use Fe^0 as the electron donor, as the BCXR theory predicts. As discussed above, sufficient acidity at the metal-biofilm interface may be required to make microbial coupling of "X-reduction" to iron oxidation possible; if initial pH is not sufficiently low, then microorganisms may need to utilize limited organics to create a localized low-pH environment (e.g. reactions 4 and 8), low pH being a factor of abiotic metal corrosion as well (Piron, 1994). Corrosion pits (Fig. 1C) may develop exactly where clusters of acidity-generating / iron-electron-consuming microbes are located.

On the other hand, if a medium is nutrient-limited, then energy for all or most microorganisms within a biofilm may be supplied through proton-dependent coupling of "X-reduction" to iron oxidation. The biofilm has to be thin enough for this and/or a syntrophic interaction has to be established to enable an efficient transfer of electrons from a metal surface to microbes located farther from the metal – biofilm interface. In the case of such a thin and relatively homogeneous biofilm, insoluble iron compounds (e.g. iron sulphide) may homogeneously cover/passivate an iron surface, and microbially influenced corrosion inhibition (MICI) may occur (Kip and van Veen, 2015; Videla and Herrera, 2009; Zuo, 2007). Thus, in this case, the situation may not progress to that described in Fig. 1C.

Despite low pH was proposed to play a role in MIC (Crolet, 1992; Crolet, 2005; Daumas et al., 1993), to the best of our knowledge, the capability of localized acidity production was confirmed only for some corrosion-aggravating SRB (Daumas et al., 1993); in addition, some methanogens were shown to have lower pH optima when the H_2 availability was limited and Fe^0 was provided, compared to their pH optima in the case of abundantly available H_2 and CO_2 (Boopathy and Daniels, 1991). Videla and Herrera (2005) mentioned the role of the localized acidity in MIC and Gu (2012, 2014) discussed how low pH established through production of organic acids by fermentative acid producing bacteria (APB) could aggravate corrosion. We propose that nutrient limitation at a metal-biofilm interface may induce activation of the enzymatic proton-producing/proton-secreting functions (i.e. those performed by hydrogenases/proton pumps) in respiratory and methanogenic microorganisms to make them capable of using Fe^0 as the electron donor. If this is true, then, in Type I MIC, iron dissolution is aggravated through both microbial utilization of electrons lost by iron and microbial acidity generation near a metal surface.

Concluding remarks

We have proposed a modification to the BCXR theory by Xu and Gu (2011) on the basis of the fact that coupling of "X-reduction" to iron oxidation is always proton-dependent (reactions 3, 6, 7 and 9) and on the basis of findings by Daumas et al. (1993) and by

Boopathy and Daniels (1991) demonstrating that some iron-oxidizing microorganisms need low pH for utilization of electrons derived from iron and may be capable of pH-regulation. Our assumption is that iron-oxidizing XRP are capable of generating acidity locally at a metal – biofilm interface to enable themselves to use Fe⁰ when they experience shortage of organic electron donors. We also propose that biofilm thickness may be a factor of MIC/MICI. Additional evidence is required to confirm these assumptions. Experiments involving complex measurements using microelectrodes, microsensors, microprobes, gas chromatographs, scanning electron microscopes (SEM), confocal laser scanning microscopes (CLSM), atomic force microscopes (AFM) etc., combined with transcriptomics analyses, are, particularly, required. Having proven that the iron-oxidizing XRP's capability to generate acidity locally at a metal – biofilm interface is a common phenomenon would mean that microbial acid production is pertaining to both Types I and II MIC.

References

- Boopathy R., Daniels, L., 1991. Effect of pH on anaerobic mild steel corrosion by methanogenic bacteria. *Applied and Environmental Microbiology* 57, 2104-2108.
- Cord-Ruwisch, R., 2000. Microbially influenced corrosion of steel. In: Lovley, D.R. (Ed.), *Environmental microbe-metal interactions*. ASM Press, Washington, DC, pp. 159-173.
- Crolet, J.-L., 1992. From biology and corrosion to biocorrosion. *Oceanologica Acta* 15, 87-94.
- Crolet, J.-L., 2005. Microbial corrosion in the oil industry: a corrosionist's view. In: Ollivier, B., Magot, M. (Eds.), *Petroleum Microbiology*. ASM Press, Washington, DC, p. 378.
- Daniels, L., Belay, N., Rajagopal, B.S., Weimer, P.J., 1987. Bacterial methanogenesis and growth from CO₂ with elemental iron as the sole source of electrons. *Science* 237, 509-511.
- Dinh, H.T., Kuever, J., Mussmann, M., Hassel, A.W., Stratmann, M., Widdel, F., 2004. Iron corrosion by novel anaerobic microorganisms. *Nature* 427, 829-832.
- Daumas, S., Magot, M., Crolet, J.-L., 1993. Measurement of the net production of acidity by a sulphate-reducing bacterium: experimental checking of theoretical models of microbially influenced corrosion. *Research in Microbiology* 144, 327-332.
- Dronen, K., Roalkvam, I., Beeder, J., Torsvik, T., Steen, I.H., Skauge, A., Liengen, T., 2014. Modeling of heavy nitrate corrosion in anaerobe aquifer injection water biofilm: a case study in a flow rig. *Environmental Science and Technology* 48, 8627-8635.
- Eklund, G.S., 1974. Initiation of pitting at sulfide inclusions in stainless steel. *Journal of the Electrochemistry Society* 121, 467-473.
- Enning, D., Garrelfs, J., 2014. Corrosion of iron by sulfate-reducing bacteria: new views of an old problem. *Applied and Environmental Microbiology* 80, 1226-1236.
- Flemming, H.-C., Wingender, J., 2010. The biofilm matrix. *Nature Reviews Microbiology* 8, 623-633.
- Gu, T., 2012. New understandings of biocorrosion mechanisms and their classifications. *Journal of Microbial and Biochemical Technology* 4: iii-vi.
- Gu, T., 2014. Theoretical modeling of the possibility of acid producing bacteria causing fast pitting biocorrosion. *Journal of Microbial and Biochemical Technology* 6: 68-74.
- Huang, C.-P., Wang H.-W., Chiu, P.-C., 1998. Nitrate reduction by metallic iron. *Water Research* 32, 2257-2264.
- Kane, R.D., Cayard, M.S., 1998. Roles of H₂S in the behavior of engineering alloys: a review of literature and experience. *Corrosion (NACE International)*, paper #274.

- Kip, N., van Veen, J.A., 2015. The dual role of microbes in corrosion. *The ISME Journal* 9, 542-551.
- Lin, K.-S., Chang, N.-B., Chuang, T.-D., 2008. Fine structure characterization of zero-valent iron nanoparticles for decontamination of nitrites and nitrates in wastewater and groundwater. *Science and Technology of Advanced Materials* 9, 025015.
- Lino, T., Ito, K., Wakai, S., Tsurumaru, H., Ohkuma, M., Harayama, S., 2015. Iron corrosion induced by nonhydrogenotrophic nitrate-reducing *Prolixibacter* sp. strain MIC1-1. *Applied and Environmental Microbiology* 81, 1839-1846.
- Ma, H., Cheng, X., Li, G., Chen, S., Quan, Z., Zhao, S., Niu, L., 2000. The influence of hydrogen sulfide on corrosion of iron under different conditions. *Corrosion Science* 42, 1669-1683.
- Olsson, C.-O.A., Landolt, D., 2003. Passive films on stainless steels – chemistry, structure and growth. *Electrochimica Acta* 48, 1093-1104.
- Park, H.S., Chatterjee, I., Dong, X., Wang, S.-H., Sensen, C.W., Caffrey, S.M., Jack, T.R., Boivin, J., Voordouw, G., 2011. Effect of sodium bisulfite injection on the microbial community composition in a brackish-water-transporting pipeline. *Applied and Environmental Microbiology* 77, 6908-6917.
- Piron, D.L., 1994. *The electrochemistry of corrosion*. NACE Press, Houston, TX.
- Stewart, P.S., 2003. Diffusion in biofilms. *Journal of Bacteriology* 185, 1485-1491.
- Thauer, R.K., Kaster, A.-K., Goenrich, M., Schick, M., Hiromoto, T., Shima, S., 2010. Hydrogenases from methanogenic archaea, nickel, a novel cofactor, and H₂ storage. *Annual Review of Biochemistry* 79, 507-536.
- Thauer, R.K., Stackebrandt, E., Hamilton, W.A., 2007. Energy metabolism and phylogenetic diversity of sulphate-reducing bacteria. In: Barton, L.L., Hamilton, W.A. (Eds.), *Sulphate-Reducing Bacteria: Environmental and Engineered Systems*. Cambridge University Press, UK, pp. 1-37.
- Till, B.A., Weathers, L.J., Alvarez, P.J.J., 1998. Fe(0)-supported autotrophic denitrification. *Environmental Science and Technology* 32, 634-639.
- Videla, H.A., Herrera, L.K., 2005. Microbiologically influenced corrosion: looking to the future. *International Microbiology* 8, 169-180.
- Videla, H.A., Herrera, L.K., 2009. Understanding microbial inhibition of corrosion. A comprehensive overview. *International Biodeterioration and Biodegradation* 63, 896-900.
- Von Wolzogen Kühr, C.A.H., van der Vlugt, L.S., 1934. The graphitization of cast iron as an electrobiochemical process in anaerobic soil. *Water* 18, 147-165.
- Xu, D., Gu, T., 2011. Bioenergetics explains when and why more severe MIC pitting by SRB can occur. *Corrosion (NACE International)*, paper #11426.
- Xu, D., Li, Y., Song, F., Gu, T., 2013. Laboratory investigation of microbiologically influenced corrosion of C1018 carbon steel by nitrate reducing bacterium *Bacillus licheniformis*. *Corrosion Science* 77, 385-390.
- Zuo, R., 2003. Biofilms: strategies for metal corrosion inhibition employing microorganisms. *Applied Microbiology and Biotechnology* 76, 1245-1253.

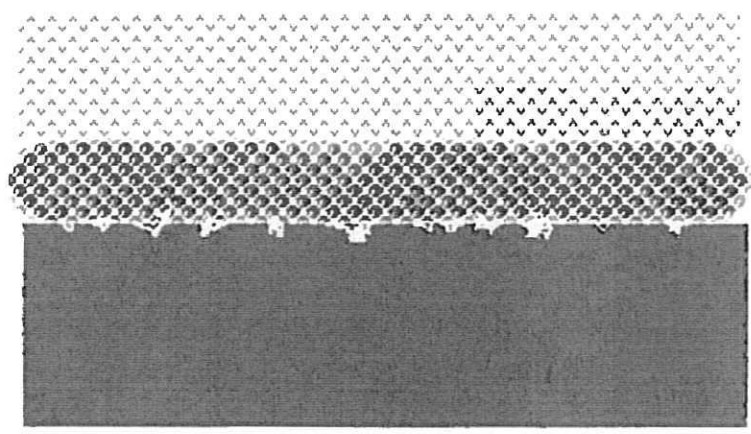
Figure captions

Fig. 1. Proposed stages in Type I MIC: **(A)** A thin biofilm on the metal (iron/steel) surface in an aqueous or gaseous medium; in a nutrient-limited medium, the biofilm may remain thin and relatively homogeneous to allow an access to Fe^0 as a source of electrons to all microorganisms within the biofilm; although microbial acidity generation is expected to occur at the metal-biofilm interface and iron is expected to be oxidized, relative homogeneity of the biofilm may be reflected in relatively homogeneous covering of the metal surface with the product of its oxidation (e.g. iron sulfide), which may be passivating, i.e. MICI rather than MIC may occur; in a nutrient-rich medium, the biofilm may grow thicker and heterogeneous **(B)**, having clusters of microbes, which are insufficiently supplied with organic nutrients and which, to enable themselves to use electrons derived from Fe^0 as a source of energy, generate sufficient acidity at the metal-biofilm interface; accelerated iron dissolution due to iron-electron-consuming and acidity generation microbial activities in the areas where such clusters are located may lead to pitting corrosion **(C)**.

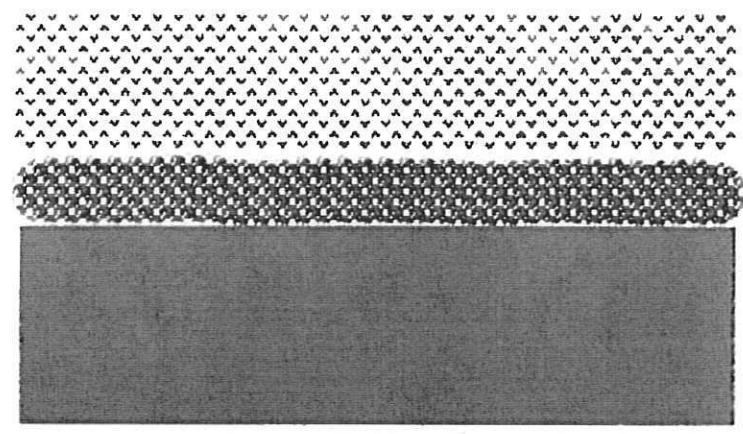
aqueous or gaseous medium

biofilm

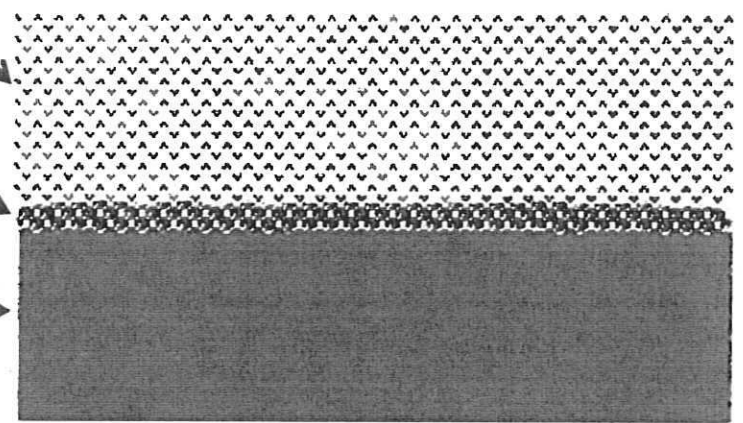
metal



C



B



A