

Surface-Charge Mobility Theory - An Explanation for Certain “Microwave Effects”

Ed Ripley

Consolidated Nuclear Security, LLC, Y-12 National Security Complex

E-mail: edward.ripley@cns.doe.gov

Microwave heating mechanisms are generally well defined and understood. It is widely known that many materials heat efficiently in microwave fields. For many materials, microwaves penetrate to a significant depth for rapid volumetric heating of the material. However, the heating mechanisms for heating metallic and other electrically conductive materials is less widely understood.

The ability of finely divided metal powders to heat from room temperature to very high temperatures has been widely documented.^{1,2} Bulk metals and other conductive materials are reflective to microwaves at room temperature, penetration of microwaves is limited to the surface, and these materials resist heating from room temperature to some elevated temperature, at which point the metals will actually start to absorb and heat in a microwave field.³

The question of why powdered metal heats easily from room temperature, however resists heating in a bulk form is not a simple question to answer. The heating of metals has been attributed to ohmic heating, magnetic/ferromagnetic effects, and eddy currents. Reports indicate that the magnetic (H field) or the electrical (E field) was responsible for heating a material. These observations did not provide adequate explanations for the heating mechanism in other metals systems.⁴

While each of these explanations may be adequate to explain heating of a particular metal, they are not adequate to explain the heating behaviors observed in all cases. What follows is a view of what is happening at the surface of materials that are electrically conductive, and thus generally reflect microwaves very efficiently. In addition to explaining the heating behaviors observed in metal, this theory also explains other phenomena such as enhanced surface diffusion, activation and passivation of surfaces, and the

drastically increased rates at which chemical reactions occur at the surface of conductive materials in even modest microwave fields. Many times the reactions occur on a scale or at rates which cannot be justified using standard chemistry and chemical kinetic models.⁵⁻⁷

The Y-12 National Security Complex has been researching these topics since the late 1990s, and has developed their microwave melting and casting processes, enhanced diffusion and rapid de-passivation, and investigated enhanced corrosion of aluminum in microwave fields.^{6,8,9}

In a metal system, individual electrons are not associated with the individual metal atoms but are shared within the atoms in the system. Metallic bonds are formed between atoms where the bonds are formed as an electromagnetic interaction between delocalized electrons called conduction electrons and the metallic nuclei within the metal system. This can be pictured as the sharing of “free” electrons in a lattice of positively charged metal ions.

Delocalized electrons are those electrons in a molecule that are not associated with a single atom or covalent bond. Delocalized electrons are contained within an orbital that extends over several adjacent atoms. The electrons in a metal system are delocalized and contribute to the properties of the metal. Delocalized electrons are free to move in all directions throughout the metallic structure and give rise to properties such as conductivity.

This model is a good approximation for all the atoms in the system except those at the surface. When the delocalized electrons reach the surface of the metal system, they cannot continue in all directions, rather they can only remain on or near the surface, or return to the bulk. In either case, there are an abundance of delocalized electrons at the surface of the metal. In essence, these electrons

are exposed, and thus are vulnerable to influences by outside forces.

If an electromagnetic wave, such as a microwave, passes over the surface, it can cause a short range, localized, disequilibrium of electrons at the surface to occur. The electrons are swept across the surface like sweeping water across a tennis court with a squeegee. In the area in front of the electromagnetic wave, the electrons pile up. In the area behind the wave, momentarily there is a localized absence of electrons.

This theory was called “surface charge mobility” because the electromagnetic energy only seemed to affect the distribution of the delocalized electrons at the surface.⁸ Electromagnetic radiation like microwaves generally only directly influence the electrons at the exposed surface. The effects usually do not penetrate deeply to a sufficient depth to directly affect the bulk material. However, phenomena such as bulk chrome diffusion in steel, ohmic heating and the instances where metals heat better in H fields, as well as when the E and H fields have the same heating effect, can all be described using surface charge mobility.

In the case of an individual particle of metal without any microwave influence, we can visualize it as having a number of electrons that travel from the bulk to the surface, and once on the surface, return to the bulk. This constant shuffling and rebalancing of the surface electrons can be shown in the example in Figure 1a. There is a general equilibrium balance of electrons at the surface. It is important to note that for these examples it can be assumed that there is little or no change to the electronic structure of the atoms, beyond the first few surface atoms. The example in Figure 1b shows a short term displacement of the surface electrons in the presence of a microwave field where the electrons get swept back and forth across the surface and will at some point result in electrons momentarily displaced at the surface.

Multiple metal particles are pictured without the presence of a microwave field in Figure 2a below. Where the surface electrons are being momentarily influenced by a common electromagnetic field, the resulting surface charge is like 2b. In this case the instantaneous net positive

charge is adjacent to a net negative charge in a nearest neighbor particle.

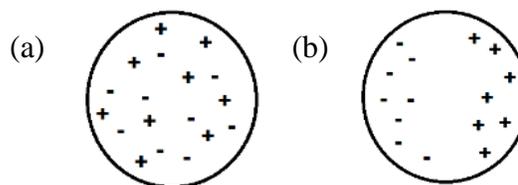


Figure 1. (a) A representation of electrons (-) and open sites (+) on a metal particle without any MW influence. (b) The same particle as a MW passes over the surface, sweeping surface electrons momentarily to one side of the particle.

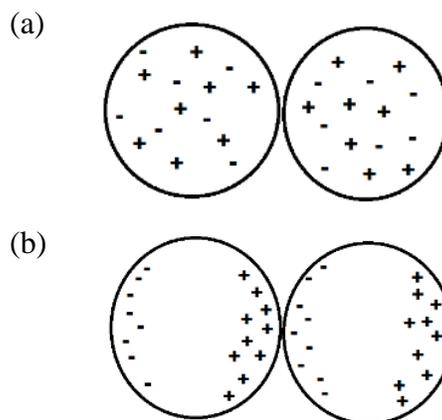


Figure 2. Representation of metal particles without any MW influence (a) and the same particles when a MW passes over the surface (b), resulting in a momentary charge imbalance giving rise for the opportunity to charge transfer between the particles.

This phenomenon is consistent with observation. Many researchers have reported arcing between powder particles while microwave sintering. When the field is reversed, the electrons are swept to one side of the particle. The charge imbalance results in another charge transfer between adjoining particles. As this occurs between particles, an intense localized heat is generated between the particles at the point of contact, and this heat could cause localized melting, fusion of the particles, and eventually necking and sintering of the materials. This is also consistent with observation.¹⁰

If the net surface area is increased (by decreasing the size of the particles), the net amount of electrons which could be influenced by the microwave field would increase as a function of surface area. Thus, the magnitude of charge transfer and the resulting heat generation would

increase. This is also consistent with observation.^{1,2,3} An additional factor is that the charge field surrounding the particle is governed by the scaling law: The particle charge field increases as $\sim 1/r^3$, hence, the smaller the radius, the higher the resulting charge field. This, in combination with the increased surface area for the smaller particle size and the increased opportunity for MW influence, results in behavior for small particles that is quite different from the bulk material as a larger solid.

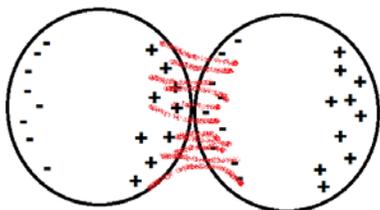


Figure 3. When the charge imbalance is greater than the breakdown potential of the junction or gap between the particles, the electron transfer occurs resulting in localized heating at the junction between particles.

The arcing between the particles results in intense localized temperature increase at the point of contact between the particles, and a small bridge forms where the particles are welded together. When the electrons move, all have to crowd through a small electrical bridge, and just like a fuse which heats up when current is passed through a small conductor, it heats up. This heating can result in the necking, and sintering observed after the metal component apparently stops its initial micro-arcing. As the temperature of the metal increases, two new processes start having an increasing effect. The metals themselves will start to couple with the microwave fields at elevated temperatures.³ In addition, the greater resistance to electrical conduction because the metal is hot causes increased heating in the already hottest parts. Depending on the material, the motion of the surface electrical fields can build up induced currents in the bulk. To further complicate these heating effects, the H and E fields will result in different levels of heating in materials which have a magnetic moment, are diamagnetic, or are ferromagnetic.

Heating of metals in electromagnetic fields depends on the shape and size of the metal, the electrical conductivity/resistivity of the metal (at

room temperature and elevated temperatures), and the magnetic (diamagnetic, paramagnetic, ferromagnetic) properties of the metal. The heating can be caused by:

- Simple arcing
- Ohmic heating
- Induced eddy currents
- Resistive heating
- Direct coupling

The mechanisms and combinations of these heating methods can be combined in a number of ways depending on the previously mentioned parameters.

Further complications arise from the intense localized heating between particles, which results in an under-reporting of the bulk temperatures of the metal. The temperatures where the metal is arcing, fusing, and sintering is, many times, very high even though the bulk temperature gets under reported. For this reason, it has been widely reported that sintering occurs at a lower temperature in microwave fields than by conventional heating.^{2,11,12} Thus, the temperature where the sintering and/or melting is occurring is in fact at the sintering/melting point, even though the bulk temperature when measured optically or by contact methods is lower.

It might seem that these “microwave effects” would be limited to applications where powders and compacted parts are placed in a microwave field. However, many other interesting phenomena are occurring when bulk metal parts are placed in microwave fields. The surface charge mobility model, which describes the effect of microwaves on the bulk of metals as a sweeping of electrons at the surface, has a profound effect on the chemical activity of the surface as well as the structure of the crystalline lattice for the first few atoms at the surface. These two processes can give rise to some unexpected results.

The size of the atoms and the electron configurations within the metal system determine the inter-atomic spacing and the resulting crystalline structure. At the surface, if all the electrons were momentarily swept from a portion of the surface, it could be inferred that the inter-atomic spacing of the lattice could be dilated or contracted depending on the magnitude of the

imbalance. This would, in essence, give rise to a short duration, short order dilation of the lattice spacing as a result of the momentary sweeping away and piling up of mobile electrons at the surface. This should result in a change in the chemical reactivity or the surface as well as properties associated with the lattice structure. These properties are the diffusion and inter-diffusion constants. The localized dilation and constriction of the interatomic lattice spacing near the surface can lead to reductions of the energy required for an atom at the surface to diffuse into the surface, as seen in the region of Figure 4 indicated by the widening of the inter-atomic lattice spacing (+).

Fick's law predicts the rate of diffusion of one type of atom into another. Changes in the lattice spacing could greatly affect the energy required for diffusion to occur. By comparing the predicted and actual rates of diffusion in electromagnetic fields, it is possible to calculate an inter-diffusion constant in electromagnetic fields and use this value to calculate the change (dilations, and contractions) in the inter-atomic spacing.

For active diffusion to occur, the temperature must be sufficiently elevated to overcome the energy barriers to atomic motion.¹³ Atoms are constantly in motion with $\sim 10^{13}$ vibrations per second. Heat causes the atoms to vibrate, and the amplitude increases with temperature until the vibrational energy is sufficient to break the atomic bonds and the metal melts. The energy of the atom due to thermal excitation is on the order of kT , with an average energy $P(E) \sim \exp(-E/kT)$, where, k is the Boltzmann's constant (1.38×10^{-23} J/K or 8.62×10^{-5} eV/K), and T is the temperature in Kelvin.

If what has been previously discussed holds true, in addition to the vibrational energy from thermal sources, if we were to add the vibrational energy caused by displacing the delocalized electronic structure of the surface atoms, then we see that the diffusional energy required to penetrate the first few surface atoms is decreased significantly.

$$D \approx \frac{d^2 \nu}{3} \exp\left(\frac{-Q}{RT}\right)$$

where d is the interatomic spacing, ν is the vibrational frequency, and Q is the activation energy.¹⁴

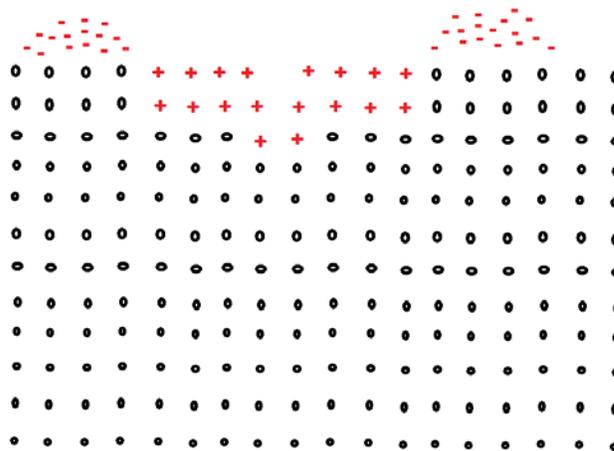


Figure 4. Graphic representation of outer orbital electrons being temporarily displaced by the presence of a MW field passing over the surface of a metal. Notice the slight distortion of the lattice caused by charge-induced strain at the surface.

Increased diffusion rate of chrome into steel was observed by Stan Morrow et al.⁶ The mechanism, description of the processes involved, and their conclusions may not be entirely accurate; however, their results are in strong agreement with surface charge mobility theory and the resulting predictions. If we look at the diffusion process as two separate steps, first the association of the chemical species with the surface, called the “boost” phase, and the second which is simple Fick's law diffusion, the rates of both of these processes are increased in a microwave field, and are consistent with the theory described previously.

An example of the dramatic differences between diffusion of chrome in iron is illustrated below, with a 20% concentration of Cr into Fe at a depth of 0.02 cm. The time required is 70 hours. The same concentration at the same depth and at the same temperature requires only 1 hour in a microwave field, hence the presence of the microwave field increases the diffusion constant of Cr into Fe by a factor of x70 to $2.49 \times 10^{-12} \text{ m}^2\text{S}^{-1}$.

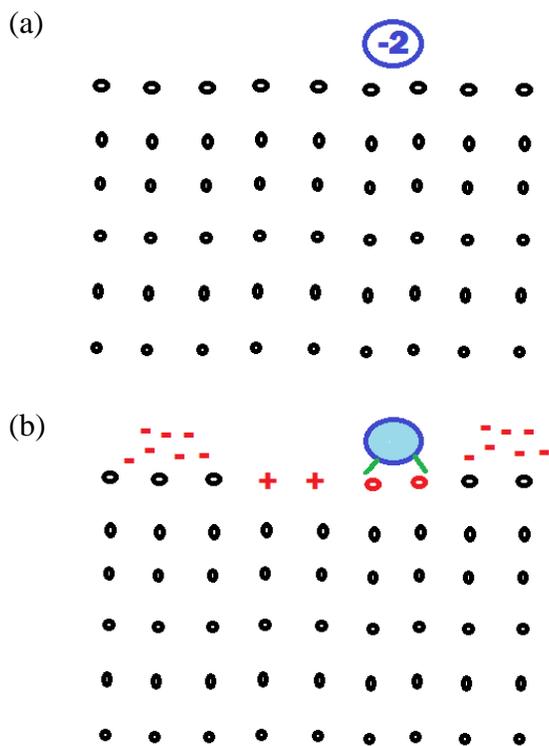


Figure 5. (a) A chemical species at the surface of the metal with no MW field present during the “boost” phase of diffusion. 5b shows the chemical bond which results from the presence of a MW field temporarily displacing the outer orbital electrons, resulting in a temporary positive charge.

This new value for the diffusion coefficient indicates a more rapid diffusion than can be accounted for by simply taking into account the increased reaction time for the boost reaction and the vibrational frequency of the atoms in the unit cells at the surface of the metal. The final part was obtained by removing 5 of the 6 degrees of freedom in the random walk calculations in the diffusion reaction. This is justified because one degree of freedom (the surface) is eliminated because the site is occupied by the chemically bonded diffusing species. Four more degrees of freedom are eliminated when the first few surface interstitial sites saturated, which occurs very quickly. Now a high diffusivity path is established where the random walk calculation has only one degree of freedom, and that is to diffuse into the bulk. When the vibrational energy and the elimination of degrees of freedom in the random walk are accounted for, the mathematics for the increased rate of diffusion is satisfied. Now the larger value of the diffusion constant not only agrees with

experimental observation, but also makes sense from a diffusional, chemical kinetics, and thermodynamic perspective.

If a species which requires a net positive charge to chemically combine with the surface is in proximity with the surface as the electrons at the surface are swept away, for a brief moment a strong net positive charge exists. Chemical reaction is a function of probability and kinetics; however, this could strongly effect the rate of both. Conversely, if a net negative charge is required to cause chemical bonding between the chemical species and the metal surface, this also occurs when the electrons are swept across the metal surface, resulting in a momentary excess of electrons at the surface. In both cases the rate and probability of reaction increase dramatically in the presence of an electromagnetic field such as MW. This process occurs at a high rate. For example, household microwave frequencies (2.45 GHz) occur 2.45 million times a second. If this is factored into both the chemical kinetics associated in the boost phase of the process, and into the diffusion portion of the equation, it is within an order of magnitude agreement with observation. It also occurs at a rate far in excess of either chemical kinetic predictions or Fick’s law behavior.

The combination of these two effects have significant practical benefit. If the electrons are in fact being moved over the surface of the metal system and creating short lived situations at the surface, where there are an abundance or absence of electrons, then chemical reactions that normally do not occur or occur slowly should be accelerated by the increased surface activity. We have anecdotal evidence that this is happening because reactions that occur slowly under certain atmospheric and temperature conditions are accelerated in even modest microwave fields. Secondly if the inter-atomic spacing were being momentarily affected at the surface then we would expect that there would be a change in the amount of energy required to overcome the potential well and diffuse into the surface. In fact, we have seen cases where diffusion of a second species into a metal occurred at many times the rate that can be explained by Fick’s law behavior. We can only assume that when the inter-atomic lattice is dilated,

even monetarily, that the diffusion coefficient is lowered by some amount.

To further amplify this effect, if a species which is bound at the surface diffuses from the surface into the bulk, a vacancy opens up on the surface for a new molecule to bind to that site. When this chemical reaction at the surface occurs, it removes one degree of freedom from the random walk scenario and further enhances the process of diffusion. But more importantly it influences the direction of the diffusion by removing one of the possible directions which diffusion can occur.

In fact, although this has never been conclusively proven, the anecdotal evidence from processing a metal sample in a given set of conditions has been observed. In a given set of thermal conditions and processing conditions, a diffusion experiment was conducted to diffuse chrome into iron and steels. The experiment was repeated under the same conditions with the addition of 2.45 GHz microwaves, and the amount of chrome diffusion in the microwave field was significantly improved.

The chrome diffusion using the thermal process alone in a 72-hour heating cycle was significantly less than the chrome diffusion under the same thermal and atmospheric conditions for 1 hour in a microwave field. Not only was the improvement astounding from a processes improvement standpoint, but the resulting chrome diffusion was greater than should be possible with Fick's law behavior, assuming the same constant diffusion coefficient.

The implication is that these phenomena are occurring as postulated. However, the dilation and constriction of the interatomic spacing of the atoms at the surface as a response to MW fields is very difficult to prove. These phenomena would only affect the surface atoms; however, the results could certainly establish a high diffusivity path, and affect the diffusion rate in the bulk. Assuming that a chromium ion reacts with the surface occupying a site on the lattice when the MW passes over the surface and causes small dilations and contractions of the surface atoms, the potential energy required to diffuse into the surface would cyclically increase and decrease at 2.45 billion cycles per second. Giving a large number of opportunities to diffuse

into the surface, once inside the metallic lattice, there is a potential for the chromium to move in any one of the six available directions. However, with the high surface charge mobility, the probability of a chromium reacting at the surface is high. This removes one of the possible directions for the diffusing species. When the chromium in the metal lattice does move to a new position, then the surface chromium ion has a high probability of diffusing from the surface into the metal lattice, which leaves an available bonding at the surface.

From a practical sense, within a few seconds the available sites at the surface and within the first few lattice positions become filled. This eliminates all except one degree of freedom for the diffusion to occur. These high diffusivity phenomena and high diffusivity pathways have been demonstrated and well characterized.^{6,7}

If there is a dilation and contraction of the inter-atomic lattice spacing of the metal surface when exposed to a MW field, it supports the case of high diffusivity assuming rapid boost phase and elimination of the degrees of freedom in the diffusion rate calculations. The combination of surface charge mobility causing ohmic heating at the surface and the opportunity to cause micro-arcing under a microwave field would explain the heating phenomena which is observed on the various surfaces and particle sizes of conductive materials. Previously, these materials were described as reflective; however, reflection from the surface and perturbations in the electron population are not necessarily mutually exclusive.

Surface charge mobility phenomena has not been conclusively proven; however, if the implications of these assumptions are applied in an experimental setting, the predicted behaviors will be observed.

By extending the logical implications of this model, it is possible to design structures that can exploit this short range surface charge mobility and the resulting temporary charge imbalances. One example is to use a specifically designed shape to initiate and maintain thermal plasmas without the need to use magnetic constraint to control the location of the plasma.¹⁵⁻¹⁷ Another example is the redesign of thermocouple shields to allow their use in microwave fields.¹⁸

For further reading:

1. Roy R., Agrawal D., Cheng J., Gedevanishvili S., *Nature*, **399**, 1999, 668-670.
2. Mondal A., Agrawal D., Upadhyaya A., *Journal of Microwave Power*, Jan. 2009.
3. Ripley E., Eggleston P., White T., *Proc. 3rd World Cong. MW*. 2002, 241-246.
4. Sato M., Fukushima H., Ozeki F., Hayasi T., Saito Y., Takayama S., *IEEE, 12th Joint Conf IR and mm Waves*, 2004, pp.832-832.
5. Varma, R. S., Solvent-free organic syntheses using supported reagents and microwave irradiation. *Green Chem.* 1999, **1**, 43-55.
6. US Patent 6,554,924, S. Morrow et al, *Metallic diffusion process and improved article produced thereby*.
7. Huey H., Morrow S., *Proc. 4th World Cong. MW*. 2004, 286-293.
8. Y/NB-6013, E. Ripley. Pages 14-15; 4/27/2001.
9. Y-12, Internal Memo, E. Ripley, RE: IMPI conference San Francisco, 4/24/2001.
10. Sun J., Wang W., Yue Q., Zhang J., Zhao X., Song Z., *Applied Energy*, **175**, 2006, pp. 141-157.
11. Agrawal D., *JOM*, **Vol 19** (4, 5 & 6), 1997.
12. Chhillar P., Agrawal D., Adair J., *Powder Metallurgy*, **51**, 2008, pp.182-187.
13. Callister W., Rethwisch D. *Materials Science and Engineering: an introduction*, 9th edition. Wiley, 2013.
14. W. Jost, *Diffusion in Solids, Liquids, Gases*, Academic Press, 1960, 3rd edition.
15. US Patent 7,603,963, E. Ripley, *Controlled zone microwave plasma system*.
16. US Patent 7,909,907, E. Ripley et al, *Methods for high volume production of nanostructured materials*.
17. US Patent 8,028,654, E. Ripley, *Planar controlled zone microwave plasma system*.
18. US Patent 7,621,672, E. Ripley, *Thermocouple shield*.

About the Authors

Ed Ripley is a nuclear and metallurgical engineer, and a researcher in the Technology Development group at the Y-12 National Security Complex, where he has worked for the last 28 years. He has an MS in Nuclear Engineering and an MS in Metallurgical Engineering from the University of Tennessee. He has 25 US Patents, and has authored numerous papers, articles and chapters in four textbooks. He was the first recipient of the Y-12 Technical Fellowship, received the Y-12 Award of Excellence for his contribution to radiological instrumentation, and has received numerous Awards of Excellence from DOE and NNSA. Mr. Ripley is currently a member of the Sandia National Laboratories, Weapons Intern Program (Class of 2018). He will return to Y-12 after graduation this fall.