

Factors Affecting the Dissolution Behavior of Metals from Binary Alloys

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ABSTRACT

The strategy of recovering metals from scrap is in general much different from primary sources. One of the main differences between the treatment of scrap and that of primary sources lies with the fact that metals are frequently associated with other metals to form alloys in scrap, while metals occur in primary sources as oxides or sulfides. In this paper, factors affecting the dissolution behavior of metals from various alloy systems have been reviewed and discussed. Specific examples have been drawn from Au/Ag, Au/Cu and Ag/Cu systems. Results of the dissolution behavior of various metals from these alloys have been reviewed and compared to the dissolution behavior of single metal systems in various lixivants such as acids, cyanide and ammonia. It has been observed that the presence of other metals in alloys would significantly affect the dissolution rate of the metal in question. The leaching behavior of metals from homogeneous alloys relies on the chemical interaction between atoms in the lattice of the alloys, while that from heterogeneous alloys is affected by galvanic interaction established in the solution. The manner in which the dissolution of a certain metal is influenced by surrounding metals has been discussed in terms of passive and noble nature of the metal in relation to the neighboring metals. The role of the standard electrochemical potential of these metals on the selective dissolution for a given lixiviant has also been discussed.

1. Introduction

Scrap from various sources represents an important component of the U.S. domestic as well as world supply of many metals. For example, the U. S. refinery production of silver, gold, copper and lead in 1994 was estimated at 4,000, 400, 2.23×10^6 and 1.28×10^6 metric tons respectively, of which 50%, 38%, 17.5% and 71.9% respectively were reclaimed from scrap.¹

The reprocessing of scrap has become very important because of the ever depleting grade of ores containing these metals, coupled with the growing demand of metals in the industrial nations. In addition, recycling of these metals is environmentally sensible and desirable.

The strategy of recycling of scrap is in general much different from primary sources. One of the main differences in extracting metals from secondary sources from a primary source lies with the fact that in secondary sources metals are frequently associated

with other metals in form of alloys. There are inherent and unique characteristics of leaching of metals from an environment of other metals as compared to the leaching behavior of the same metals from oxides and sulfides.

Hydrometallurgical recovery of metals is known to be efficient technology in achieving metal production from both primary and secondary sources. Hydrometallurgical processes are beneficial due to their low energy consumption, and the ability of producing high purity metals without introducing environmentally hazardous gaseous products through stacks to atmosphere. However, hydrometallurgical processing of metals from scrap requires sound understanding of the dissolution kinetics and mechanisms of metals from their alloys. Unfortunately, the field of the dissolution kinetics of alloys is one of poorly understood subjects. In this paper, factors affecting the dissolution behavior of metals from two kinds of alloy systems, namely homogeneous and heterogeneous alloys will be presented and discussed.

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2. Accessibility to the Solution Phase

Dissolution mechanisms of metals from alloys in various solutions are a complicated and complex subject simply because when more than two metals are associated together to form an alloy, the resulting properties of the alloy are frequently unpredictable and quite different from those of individual metals, in general, there are two types of alloys. One is often referred to as homogeneous alloys where metal elements are distributed uniformly in the alloy-matrix as solid solution. The other kind is known as heterogeneous alloys in which metals are segregated to form two or more distinctive phases. When the average bond energy between unlike atoms in a binary alloy is of the same magnitude as that between two like atoms, then there is no difference between the bonds, and the solution should be a random solid solution resulting in a homogeneous alloy. In addition, the size and valence of metals also play an important role in forming solid solution. In general, the size of the atoms forming homogeneous alloys is very similar. On the other hand, when the average bond energy between unlike atoms is greater than the average bonding energy of the two like atoms, segregation and precipitation will occur

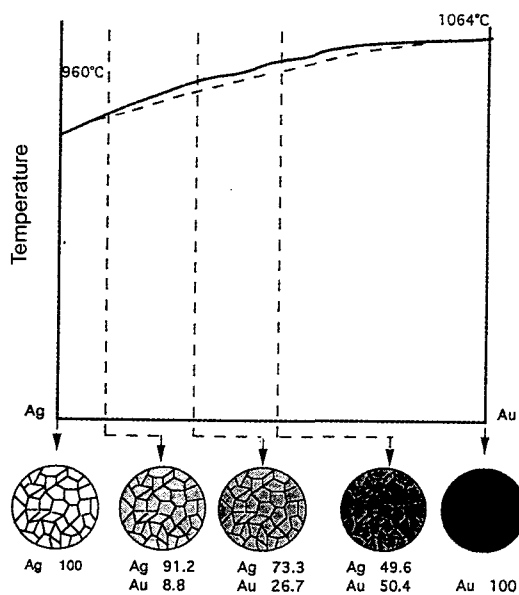


Fig. 1. Phase diagram for the gold-silver system and micrographs of alloys with varying composition.

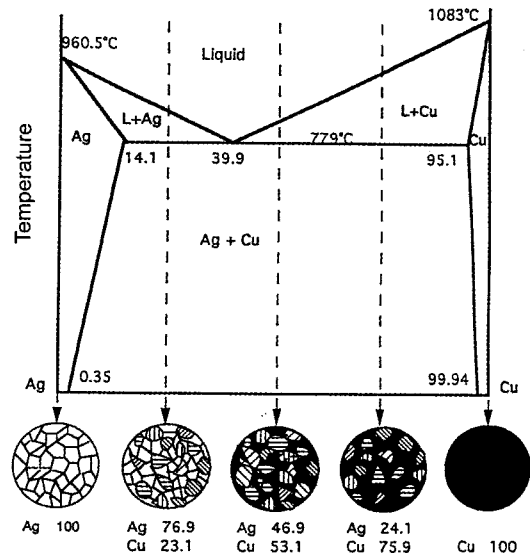


Fig. 2. Phase diagram for the silver-copper system and micrographs of alloys with varying compositions.

resulting in a heterogeneous alloy.

Good examples of homogeneous and heterogeneous binary alloys are shown in Figs. 1 and 2 representing Au-Ag and Ag-Cu systems, respectively.²⁾ As can be seen in Fig. 1, gold and silver atoms are uniformly distributed to form a single phase with different compositions along the whole x-axis. On the other hand, in Fig. 2, there are two homogeneous phases, silver-rich and copper-rich solid solutions at two narrow extreme ends. However, the wide range in the middle of the phase diagram is represented by heterogeneous phases consisting of segregated copper-rich and silver-rich phases. Scanning electron microscopic examination on Ag-Cu alloys indicated that these phases are of 10–100 microns in diameter.³⁾

There are many factors affecting the dissolution behavior of metals from homogeneous and heterogeneous alloys. First of all, the physical location of atoms in the lattice will have a significant effect on the dissolution of these metals. Fig. 3 presents three typical compositions of a binary alloy. Fig. 3-a represents a noble metal rich binary alloy in which there are far more number of noble metal atoms, B present in the lattice than less noble metal atoms, A. It is anticipated that the less noble metal atoms are more easily subjected to dissolution. In fact, the

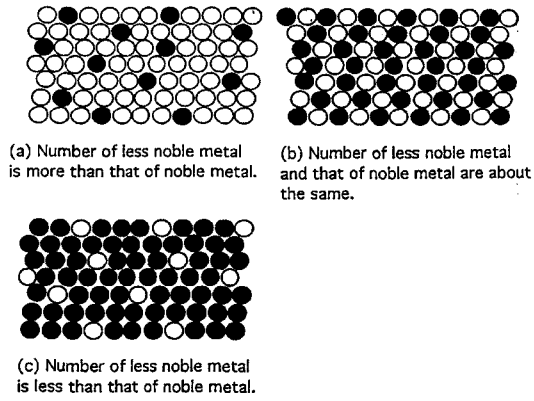


Fig. 3. Schematic diagrams showing relative numbers of more noble metal and less noble metal in homogeneous alloys. ●; less noble, ○; more noble

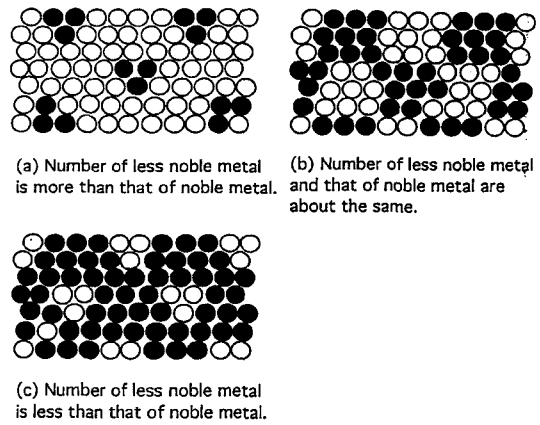


Fig. 4. Schematic diagrams showing relative numbers of more noble metal and less noble metal in heterogeneous alloys. ●; less noble, ○; more noble

chemistry of the system can be arranged that there will be a preferential dissolution of the metal A as compared to the metal B. However, when all of the atoms of A in the first layer are leached out, other A atoms in the second and subsequent layers will find themselves difficulty in getting out of the lattice and reporting to the solution phase unless there is a realignment of the atoms in these layers because atoms B are in the way to the solution phase. In other words, under these conditions, the dissolution of atoms A will be limited by the lattice diffusion process. This includes diffusion of atom A through the lattice space and diffusion of vacancies created near the solid/liquid interface toward the bulk solid phase.⁴⁾ The preferential dissolution of atom A from the lattice will be much easier in the compositions presented in Fig. 3-b and 3-c because there are enough atoms A creating continuous channels between these atoms helping access to the solution phase without relying upon the solid state diffusion. Similar behavior can also be observed with heterogeneous alloys as seen in Fig. 4.

Selective dissolution of minor constituents from alloys, therefore is almost impossible or is at best very slow. This is quite different from the normal situation with the extraction of minor elements from primary sources. In ore deposits, minor elements are frequently segregated by themselves and could be liberated during the comminution process and hence could be easily exposed to the solution

3. Nobility

Fig. 5 presents another important leaching characteristic of less noble metal A from homogeneous alloys.⁵ The y-axis represents the anodic current which is directly related to the dissolution rate of the metals associated with the alloy in question, while the x-axis is the electrode potential which is applied to the anode while it is subjected to anodic polarization. Lines (a) and (e) represent the dissolution behavior of less noble metal A and more noble metal B, respectively. As expected, in order to dissolve more noble metal, it takes a higher electrode potential (curve e) than less noble metal (curve a). However, for a binary alloy consisting of metal A and B, the dissolution behavior

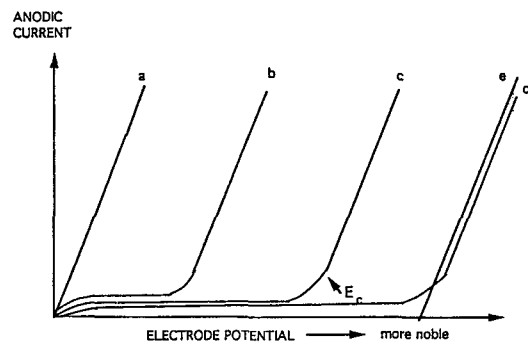


Fig. 5. Schematic illustration of the dissolution behavior of binary A-B alloys.

has two distinctive regions, namely the flat region between the initial stage of the applied potential and the critical applied potential at which the current takes off due to preferential leaching of A. This threshold potential has a special meaning for the binary alloy in that a minimum applied potential is required for a substantial amount of selective dissolution of metal A to take place. This threshold potential, often referred to as the critical potential, E_c is a function of the composition of the alloy and also a function of the solution. For example, the curve c represents an alloy in which the content of metal A is less than the alloy denoted by the curve b.

There are two types, Type I and Type II alloys in homogeneous alloy systems. These two types are determined by the presence of the relative composition of more noble metal B in the alloy. For example, in the silver-gold alloy system, when the amount of gold which is more noble metal in this alloy is less than 40 atomic percent, the alloy is referred to as Type I (Fig. 6).⁵⁾ Under this composition, a selective dissolution of metal A, in this case silver, will occur and will follow the dissolution behavior presented by curves (b) and (c) in Fig. 5. On the other hand, when the composition of gold is more than 40 atomic percent, the alloy becomes Type II and gold also dissolves as well as silver. Fig. 6 presents various alloy systems which exhibit Types I or II depending upon the presence of

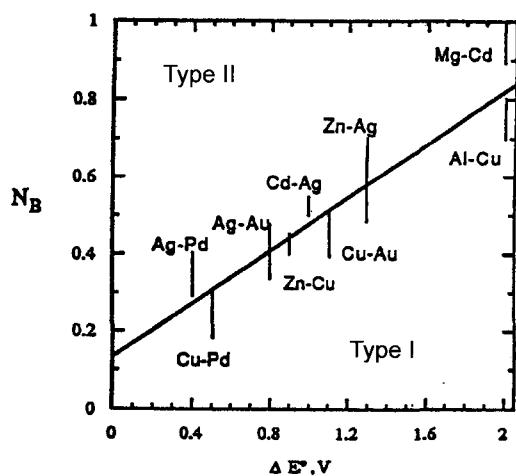


Fig. 6. A plot showing the mole fraction requirement for transition from Type I to Type II alloys.

Table 1. Standard redox electrode potentials.

Electrode	$E_{M/M+n}^{\circ}$	Electrode	$E_{M/M+n}^{\circ}$
Au/Au ⁺	1.7	Co/Co ⁺²	-0.277
Au/Au ⁺³	1.50	In/In ⁺³	-0.342
Pt/Pt ⁺	1.20	Cd/Cd ⁺²	-0.403
Pd/Pd ⁺²	0.987	Fe/Fe ⁺²	-0.440
Ag/Ag ⁺	0.799	Cr/Cr ⁺³	-0.740
Hg/Hg ⁺²	0.789	Zn/Zn ⁺²	-0.763
Cu/Cu ⁺	0.521	Mn/Mn ⁺²	-1.18
Cu/Cu ⁺²	0.337	Zr/Zr ⁺⁴	-1.53
H ₂ /H ⁺	0.00	Ti/Ti ⁺²	-1.63
Fe/Fe ⁺³	-0.036	Al/Al ⁺³	-1.66
Pb/Pb ⁺²	-0.126	Be/Be ⁺²	-1.85
Sn/Sn ⁺²	-0.136	Mg/Mg ⁺²	-2.37
Ni/Ni ⁺²	-0.250	Na/Na ⁺	-2.714

more noble metal. In general, the difference of the electro-motive forces (emf) of two metals, ΔE° , $E_B^{\circ} - E_A^{\circ}$, determines the minimum amount of the more noble metal composition required for Type II. For example, the closer the emf values of two metals are, the less the amount of more noble metal requires to affect the selective leaching of less noble metal. As can be seen in Table 1, the emf difference between silver and palladium is 0.188 volts, while that between aluminum and copper is 1.997. As a result, when the atomic percent of palladium is more than 30% in the silver-palladium alloy system, Type II prevails and selective dissolution is not possible under these circumstances. On the other hand, the atomic percent of copper could be as much as 80% before non-selective dissolution occurs in the aluminum-copper system.

4. Interatomic Interaction

The dissolution behavior of metals from homogeneous alloys is also very much dependent upon the interaction potential between metals in the lattice and their affinity with the solvent surrounding them.⁶⁻⁸⁾

The dissolution rates of gold and copper from gold-copper alloys in cyanide solutions are presented in Figs. 7

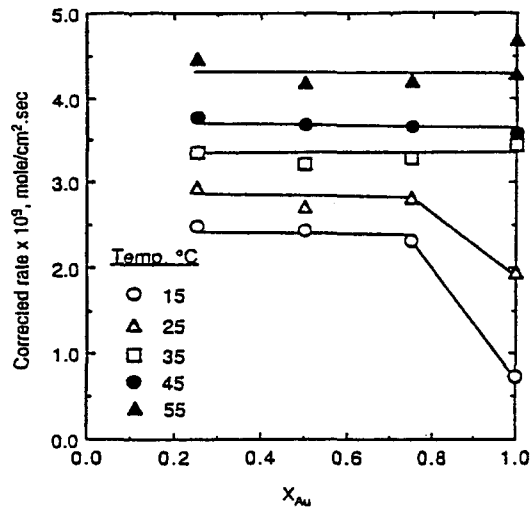


Fig. 7. Effect of composition on the gold dissolution rate at various temperatures. [cyanide conc.]: 0.02 M; disk rotation speed: 450 rpm; partial pressure of oxygen: 0.21 atm.; pH=1.0.

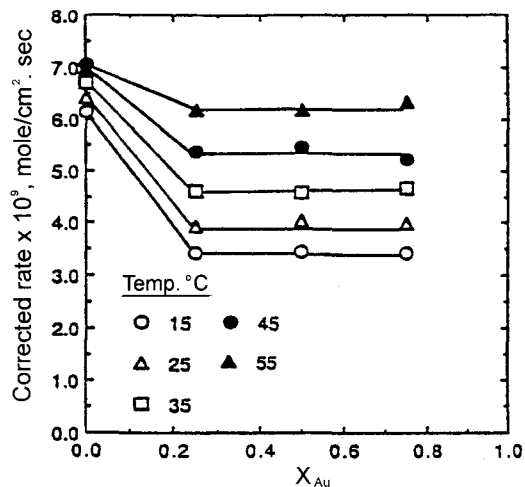


Fig. 8. Effect of composition on the copper dissolution rate at various temperatures. [cyanide conc.]: 0.02 M; disk rotation speed: 450 rpm; partial pressure of oxygen: 0.21 atm.; pH=11.0.

and 8.⁶⁾ The dissolution rate of gold is almost independent of the alloy composition at high temperatures, namely at 35–55°C. However, the gold dissolution rates of the alloys are higher than that of pure gold at low temperatures. The fact that the dissolution of gold at low temperature is low is attributed to the formation of

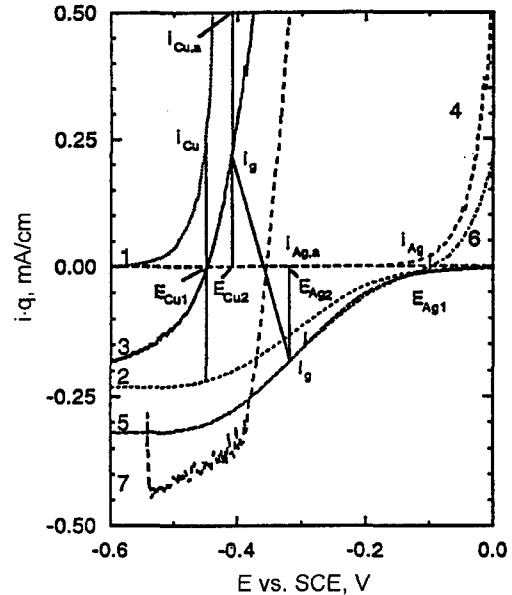


Fig. 9. Polarization curves for the dissolution of Ag-53Cu in aerated ammoniacal solutions. Temp: 25°C, disk rotating speed: 450 rpm, partial press of oxygen: 0.21 atm. [ammonia] Tot: 1.0 M. 1, anodic dissolution of Cu-phase; 2, cathodic reduction of oxygen on Cu-phase; 3, overall polarization curve of Cu-phase; 4, anodic dissolution of Ag-phase; 5, cathodic reduction of oxygen on Ag-phase; 6, overall polarization curve of Ag-phase; 7 overall polarization curve of the alloy.

passivation layer under these conditions. Under these conditions, the dissolution behaviors of pure gold and alloys are different and very much affected by the bond energies of these elements.

The chemical bond energies of Cu-Cu, Au-Au and Au-Cu are reported to be 176.4 kJ/mole, 224.9 kJ/mole and 227.8 kJ/mole.⁹⁾ Therefore, the dissolution rate of copper from pure copper metal is expected to be higher than that from copper alloys from the lattice interaction point of view. On the other hand, the dissolution rate of gold from its alloys is not much different from that of pure gold metal as long as there is no passivation at the pure gold surface.

5. Galvanic Effect

The dissolution behavior of metals from heterogeneous alloys is influenced not only by the interaction potential between similar atoms as well as dissimilar

atoms, but also by the galvanic interaction between dissimilar phases. Earlier studies indicated that the galvanic effect between two dissimilar bodies has a significant influence in the preferential dissolution.^{10,11)}

Unlike homogeneous alloy systems, in heterogeneous binary alloy systems, there will be two distinctive phases interacting with each other. For example, in the dissolution of copper and silver from a silver-copper alloy, the overall mixed potential will be a result of two mixed potentials, namely that of copper and that of silver as depicted in Fig. 9.¹¹⁾ This figure illustrates a complicated nature of the mixed potential of a silver-copper alloy, which is a net result of the mixed potential of copper and that of silver. At the dissolution potential of an alloy or the mixed potential of an alloy, E_m , the electrical charge conservation principles necessitate the establishment of the following equation.

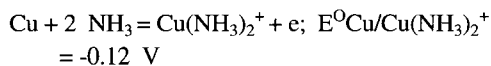
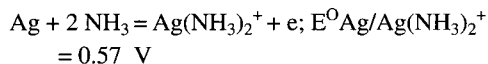
$$I_i = A_{Ag}i_{Ag,a} + A_{Cu}i_{Cu,a} = -A_{Ag}i_{Ag,c} - A_{Cu}i_{Cu,c}$$

where A , A_{Ag} and A_{Cu} are total area, and projected areas of Ag-phase and Cu-phase, $i_{Ag,a}$ and $i_{Cu,a}$ are anodic current densities of Ag-phase and Cu-phase in the alloy, $i_{Ag,c}$ and $i_{Cu,c}$ are cathodic current densities of Ag-phase and Cu-phase, $A = A_{Ag} + A_{Cu}$, and I is the total current density. The galvanic current flow between Ag- and Cu-phases can be expressed as:

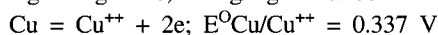
$$I_g = A_{Cu}(i_{Cu,a} - i_{Cu,c}) = A_{Ag}(i_{Ag,c} - i_{Ag,a})$$

where I_g is the galvanic current flow between the Ag-phase and Cu-phase.

According to the Ag/Cu phase diagram,²⁾ two extremely different phases exist: namely the Ag-phase and Cu-phase. The emf values for the Ag- and Cu-phases in ammoniacal solutions are¹²⁾:



and in acidic solutions are,⁹⁾



It can be seen that the emf values are much different for the Ag- and Cu-phases in the same environment. Therefore, it is expected that the galvanic coupling

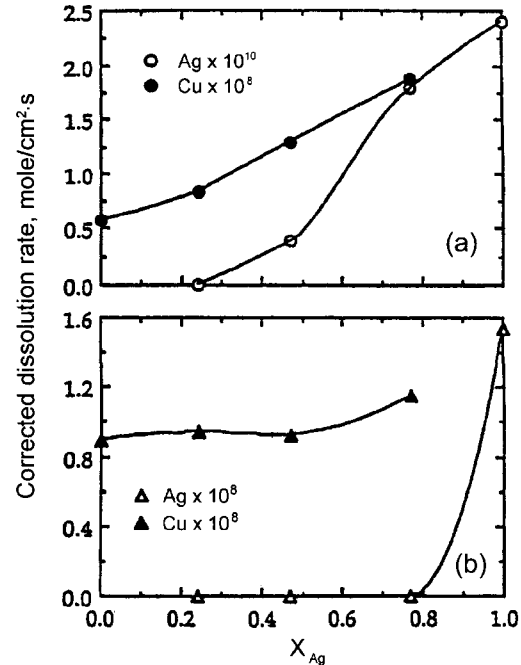


Fig. 10. Effect of composition of the dissolution rates of silver and copper from silver-copper alloys. (a) in aerated ammoniacal solutions-temp: 25°C; disk rotation speed: 450 rpm; partial pressure of oxygen: 0.21 atm.; (b) in acidic solutions-temp: 35°C; disk rotation speed: 500 rpm; [ferric sulfate]: 0.0004 M; [sulfuric acid]: 0.1 M.

effect will take place for the dissolution of silver and copper from Ag/Cu alloys.

Fig. 10 shows the effect of alloy composition on the dissolution behavior of silver and copper from Ag-Cu alloys in different leaching media.¹⁰⁾ These data clearly show that the rates of dissolution of copper from alloys are higher than that from pure copper. The dissolution rates of silver from alloys are lower compared to that of pure silver. When the composition of silver is lower than a certain limit for a given driving force, the dissolution rate of silver from the alloy is zero due to poor accessibility to the leaching media as discussed earlier.

6. Mass Transfer Effect

The dissolution of pure copper in ammoniacal solutions is often limited by mass transfer of an oxidant to the solid surface. It is interesting to note that the dissolution rate of copper from Ag-Cu alloys is

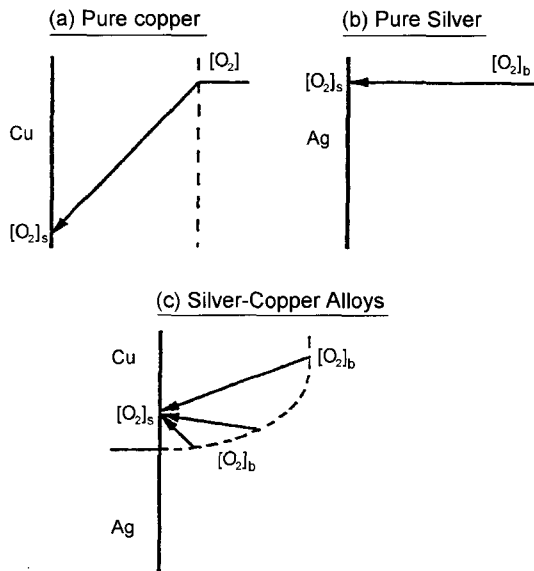


Fig. 11. Schematics showing the effect of the silver phase on the mass transfer of oxygen to the copper phase.

also mass transfer controlled. What is more interesting in this case is that the rate of dissolution of copper from these alloys is even faster than that from pure copper (Fig. 10). The reason for such an anomaly in this system is attributed to the fact that the diffusion path of oxygen from the bulk solution is shortened by the presence of the silver phase next to the copper phase. This is illustrated in Fig. 11.⁷⁾

7. Summary

The selective leaching of minor constituents from alloys is very difficult due to necessary slow lattice diffusion prior to dissolution. In homogeneous alloys, the critical potential at which selective dissolution of less noble metal takes off is very much composition and nobility dependent. The more noble metal an alloy contains, the more potential required to dissolve the less noble metal. The dissolution of the individual element in homogeneous alloys also depends upon the interaction potential between atoms.

The dissolution behavior of heterogeneous alloys, on the other hand, is affected by galvanic cell formation within the alloys during the dissolution process. The presence of more noble metal facilitates the dissolution

of less noble metal in the alloy during dissolution. When the dissolution rate of less noble metal is limited by mass transfer, the dissolution rate of the same metal in alloy system could be facilitated due to the presence of more noble metal located next to it. This is attributed to the shortened diffusion boundary layer because of very short boundary layer of the more noble metal of which rate of dissolution is chemically controlled.

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