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**Thermodynamics of Copper-Nickel
Alloys Containing Aluminum,
Silicon, Titanium, and Chromium
Relative to Their use in
Ceramic Brazing**

R. O. Williams

OPERATED BY
MARTIN MARIETTA ENERGY SYSTEMS, INC.
FOR THE UNITED STATES
DEPARTMENT OF ENERGY

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METALS AND CERAMICS DIVISION

THERMODYNAMICS OF COPPER-NICKEL ALLOYS CONTAINING ALUMINUM, SILICON, TITANIUM, AND CHROMIUM RELATIVE TO THEIR USE IN CERAMIC BRAZING

R. O. Williams

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THERMODYNAMICS OF COPPER-NICKEL ALLOYS CONTAINING ALUMINUM, SILICON,
TITANIUM, AND CHROMIUM RELATIVE TO THEIR USE IN CERAMIC BRAZING*

R. O. Williams

ABSTRACT

By varying the copper-to-nickel ratio the activity coefficients of Al, Si, Ti, and Cr can be varied over a wide range. Thus to a degree one can tailor the behavior of such alloys for usefulness in brazing ceramics. Further, considerable amounts of these active elements can be present while the ability of carbon to reduce the surface oxide film in a high-vacuum system is retained. The critical aluminum concentrations required to prevent the formation of SiO_2 , TiO , or Cr_2O_3 by reaction with Al_2O_3 are calculated. The simultaneous presence of the four active additions will presumably promote wetting without making the surface deoxidation more difficult.

INTRODUCTION

The presence of a surface film, generally an oxide, on either the base metal or the liquid braze metal greatly impedes adequate wetting in brazing. This problem is handled by either using sufficiently reducing conditions to eliminate the film or using a flux that dissolves the oxide already present. In brazing ceramics with an alloy, it seems certain that the presence of a solid film on the liquid braze metal will also prevent adequate wetting. An accepted principle to obtain wetting of a ceramic with an alloy is that of incorporating additions into the alloy that are similar to the ceramic or will react with it. Specifically, for oxide ceramics, one uses additions that form stable oxides. A consequence of such additions is that it becomes much more difficult to obtain sufficiently reducing conditions that the braze metal will not form an oxide film.

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Fluxes are seldom, if ever, used in the brazing of nonmetals with metallic brazing materials. The reason for this is simply that fluxes will generally wet the material that is to be brazed better than will the metal brazing material. Figure 1 illustrates how the flux will, under such conditions, reduce the wetting of the braze alloy. Because the braze metal wets the base metal more readily than does the flux, it will flow under the flux, as shown at the top. The braze metal has less wetting ability for a ceramic, so the presence of a flux that wets the ceramic better will reduce the wetting of the ceramic by the braze metal.

Thus, for ceramic brazing, we must resort to other agents for removing the oxide film that can form on the braze metal. As is well

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Fig. 1. In the brazing of metals the braze metal is able to flow under the flux because it wets the base metal more readily (*top*). The braze metal has a reduced capacity to wet ceramics (*middle*), and a flux will reduce the wetting (*bottom*).

known, dry hydrogen has considerable potential in this regard,¹ being regularly used in the brazing of stainless steel. But we will show that carbon has a considerably greater reducing potential.

The most expedient way of introducing the carbon is to dissolve it in the brazing alloy. It is important, however, that the alloy have the capacity to form carbides on solidification rather than graphite, which can cause loss of strength.² We will also argue that it is important that the alloy have some capacity to dissolve oxygen to promote the brazing process.

As a model system we examine Cu-Ni-base alloys that contain Al, Si, Ti, and Cr. Much of this report will apply to oxide ceramics in general, but Al_2O_3 is being considered specifically. First, we show how a considerable range of activities of these additions can be achieved. Second, we show what conditions are necessary so that the oxides of these additions can be reduced. Third, we find the minimum aluminum concentrations that are required to prevent the formation of a new oxide by the reaction of the braze metal and the Al_2O_3 .

These results should serve as a constructive guide in developing ceramic brazing alloys based on this alloy system. The problem is complex and involves many questions not addressed in this report, but we show that a substantial part of the problem can be addressed by having a thermodynamic description of the alloy system.

DEOXIDATION BY CARBON

The general reaction for the reduction of a metal oxide by carbon to form carbon monoxide can be written as

and the equilibrium partial pressure is given as

$$P_{\text{CO}} = (a_{\text{C}}/a_{\text{M}}^n) e^{-G/RT} , \quad (2)$$

where G is the change in the free energy for the reaction and a is the activity of the subscript component. The closure notation in Eq. (1) indicates that the carbon and the metal are in solution, the oxide is a solid phase, and CO is a gas.

Common metals, such as Fe, Cu, and Ni, are very easily deoxidized by this reaction and give partial pressures above atmospheric at elevated temperatures.³ Metal oxides that are used as refractories, such as Cr_2O_3 and Al_2O_3 , are so stable that the partial pressure of CO is so small that the oxides cannot be effectively reduced by this reaction.³

The activity of a component in a solution is conveniently related to its atom fraction X by the relation

$$a = \gamma X \quad (3)$$

where γ is the activity coefficient. As X approaches unity γ approaches 1, so for our present purposes we may take the activity of the base metal in an alloy to be approximately unity. For dilute alloy components γ may have a wide range of values. For additions having solubilities limited by a miscibility gap, the value of γ can be large, 100 or even larger, but in no case can the actual activity of any component exceed unity, for that would correspond to the precipitation of that component. For additions that react strongly with the base alloy, as shown, for example, by the formation of intermediate phases having high melting points, γ can be smaller than 10^{-5} . Thus reaction (1) can be used in some cases to deoxidize alloys containing Al, Cr, Si, or Ti in low to moderate concentrations, a point to be shown shortly.

The activity of carbon in an alloy saturated with carbon is unity. If the alloy is unsaturated and if the actual carbon concentration and the solubility are known, the activity is given by their ratio, since the activity coefficients for minor components may be taken to be constant. For alloys containing strong carbide formers, the carbon may be present as a carbide and the carbon has a reduced activity. In particular, the carbides that exist in the solid state will likely dissolve in the liquid. However, because carbides are normally a good deal less stable than the oxides, this is of only minor importance in the present case.

REDUCTION BY HYDROGEN

For the reduction by gaseous hydrogen,

the equilibrium pressure ratio is given by

$$P_{\text{H}_2\text{O}}/P_{\text{H}_2} = e^{-G/RT/a_M^n} . \quad (5)$$

Although this expression is very similar to Eq. (2), the fact that the reducing agent is gaseous has important consequences.

We compare the free energy change for the two reactions in reducing FeO in Fig. 2. The free energy data came from Kubaschewski and Alcock.³ At low temperatures the free energies are very similar, but at elevated temperatures the carbon reduction becomes strongly favored. This results from the facts that (1) the number of moles of gas is conserved in the hydrogen reduction, but the carbon reduction produces a gaseous product from solid components, and (2) the specific heat of a gas is greater than that of a solid.

Fig. 2. The free energy change for the reduction of FeO by H_2 and C. The specific heat of a gas is greater than that of a solid, so the driving force increases considerably with temperature for the carbon reduction. For the reduction of more refractory oxides these curves will be shifted upward, but the relative position and slopes for a specific oxide will not be sensibly changed.

These results indicate that for hydrogen reduction of FeO the ratio of H_2O to H_2 will never depart strongly from unity, but for the carbon reduction the equilibrium CO pressure at 2000 K is 1 GPa (10,000 atm). For more stable oxides, these two curves are shifted to more positive free energy values, but the relative positions and slopes are not sensibly changed because the specific heat differences are insensitive to the particular oxide being considered.

ALLOY THERMODYNAMICS

Figure 3 shows the activity coefficient versus temperature for Al, Si, Ti, and Cr for both Cu- and Ni-base alloys. The particular program and the thermodynamic formulation that were used to obtain these results

Fig. 3. Activity coefficients for Al, Si, Ti, and Cr when dissolved in liquid copper or nickel.

have been covered elsewhere.⁴ The parameters that were used are due to Kaufman and Nesor and were taken from the literature.⁵⁻¹¹ The particular way in which binary solution models are used in going to more complex systems is not uniform; the rationale for our particular formulation has been covered in detail.¹² As long as the alloys are reasonably dilute the activity coefficient γ may be assumed to be independent of concentration and not materially affected by the presence of other solutes. Further, $\log \gamma$ varies linearly with composition in going from pure Cu to pure Ni; Fig. 4 is for Ti at 1600 K. If we assume that the intrinsic wetting abilities of Cu and Ni are the same and that the contributions for the solutes are proportional to their activities, then it is evident that these four solutes would be much more effective in Cu than in Ni, and, by varying the ratio of Cu to Ni and the solute concentration, it is evident that the

Fig. 4. The log of the activity coefficients varies linearly with base composition from pure Cu to pure Ni; this plot is for Ti.

solute activities can be varied over a wide range. If the contribution of each of the solutes were the same at a given activity, then Ti and Cr would be substantially better than Si and Al in these alloys as a result of the substantially higher activity coefficients.

CARBON DEOXIDATION OF THESE ALLOYS

Because the activity coefficient of these solutes can be rather small, Fig. 3, the ease of reduction of the oxides of the solutes is drastically increased compared with that of the pure element. The partial pressures of CO have been calculated with Eq. (2) for carbon at unit activity for these solutes at 1 at. % (Figs. 5 and 6). It is readily apparent that oxides on

Fig. 5. The partial pressure of CO over the oxides SiO_2 , Cr_2O_3 , Al_2O_3 , or TiO in equilibrium with graphite and a copper alloy containing 1% Si, Cr, Al, or Ti.

Fig. 6. The partial pressure of CO over the oxides SiO_2 , Cr_2O_3 , Al_2O_3 , or TiO in equilibrium with graphite and a nickel alloy containing 1% Si, Cr, Al, or Ti.

such alloys are readily reduced at significant solute levels. The values of the CO pressures for copper alloys are substantially smaller than those for nickel alloys because the activities are larger (Fig. 3). The order of the curves is changed from Fig. 3 because the value of n in Eq. (1) differs for the different oxides. Specifically, n is 1 for TiO , $1/2$ for SiO_2 , and $2/3$ for Al_2O_3 and Cr_2O_3 .

For other solute concentrations and carbon activities the pressure ratio is given as

$$P_{CO}/P'_{CO} = a_C(100X)^{-n} \quad (6)$$

where the primed pressure corresponds to that given in Figs. 5 and 6.

REACTIONS WITH THE SUBSTRATE

Aluminum-free alloys that contain carbon could dissolve Al_2O_3 until the Al concentration became high enough in the alloy to equilibrate with the effective pressure of CO or until the carbon is depleted.

An alloy that is free of Al but contains other strong oxide formers will also have the capacity to form a new oxide by reacting with the Al_2O_3 . For Ti, for example, the reaction is

The activity of Al in the alloy that is required to cause the reaction to cease is given as

$$a_{\text{Al}} = a_{\text{Ti}}^{3/2} e^{-G/RT}, \quad (8)$$

where G is the free energy for the reaction at unit activities. Similar relations have been derived for Si and Cr, and the results are given in Table 1. It is immediately apparent that a Ti alloy must contain an appreciable amount of Al to prevent the formation of TiO, whereas only small amounts are required to prevent the formation of SiO_2 and Cr_2O_3 . In the case of Ti and Si the calculations somewhat underestimate the tendency to form new oxide phases because there is an oxide that contains both Al

Table 1. Concentration of aluminum in the alloy required to prevent the formation of new oxide at the interface at 1700 K

Alloy base	Solute mole fraction	Al mole fraction for each solute		
		Ti	Si	Cr
Ni	0.01	0.0025	0.001	1.3×10^{-6}
	0.10	0.079	0.005	1.3×10^{-5}
Cu	0.01	0.036	2×10^{-6}	6.6×10^{-6}
	0.10	>1.0	1.4×10^{-5}	6.6×10^{-5}

and Ti or Al and Si. The oxide of Cr is soluble in the Al_2O_3 so the alloy would not form an oxide having a new structure. Thus, even if regions existed that were Cr_2O_3 rich, such regions are not necessarily separated from the Al_2O_3 by a grain boundary.

DISCUSSIONS

Although a number of metals will form solid hydrides, all are unstable at temperatures below the metal melting points. Hence, hydrogen can be used as a gaseous atmosphere at elevated temperatures for all metals and alloys. This also means that a brazing alloy that contains a hydride will have limited use as a hydrogen source because the hydride will decompose before the alloy melts. In contrast, the carbides are more stable, so it is not practical to use an atmosphere that contains carbon, as methane, in most cases. This may be contrasted with the case of steels, where one may use a complex mixture that will have a controlled carburizing potential while maintaining an oxide-free surface. The consequence of the differences between hydrogen and carbon reduction is that, for the present purposes, one would use a hydrogen-containing atmosphere for hydrogen reduction but would use either an inert atmosphere or a vacuum for carbon reduction, with the source of the carbon being the brazing alloy itself.

A comment on the related process in which carbon is removed from iron by the use of wet hydrogen is in order. Here the important reaction is that of forming CO , CO_2 , and H_2 from the carbon and water vapor. The purpose of the hydrogen is primarily to maintain sufficiently reducing conditions that no oxide forms; otherwise the rate is drastically reduced.

Hydrogen atmospheres can certainly be maintained sufficiently dry that rather reactive alloys can be reduced. In particular, we heated a nickel-base alloy containing more than 10 at. % Al in hydrogen that was continuously dried with a liquid nitrogen trap, and were able to obtain an oxide-free surface.¹³ This means that even nickel-rich Ni_3Al could be maintained oxide free under such conditions. Of course, it is well known that stainless steels can be treated in dry hydrogen without the formation of a chromium oxide film.¹

We have already shown that the considerably greater potential for reduction by carbon can exist because of the greater driving force. This is further increased because maintaining a lower CO pressure in a good vacuum system is more practical than maintaining a partial pressure of H_2O in a hydrogen system.

It is reasonable to believe that the rate of oxygen removal for carbon reduction will often be limited by the surface reactions, whereas for hydrogen reduction the rate will probably be controlled by how fast the H_2O can be removed from the atmosphere and will much less likely be controlled by surface reactions.

If the removal is controlled by the rate of transport of H_2O and CO, then the rate of carbon reduction should be many orders of magnitude faster than that of hydrogen reduction because of the faster transport at a given partial pressure in a vacuum system.

Two other topics relate to the problem. Self-fluxing systems are possible; the copper-phosphorus brazing alloys are an important example.¹ Here the phosphorus is selectively oxidized to form liquid P_2O_5 , which can dissolve the other oxides. Many commercial brazing alloys contain boron, which will furnish B_2O_3 , which is also a useful fluxing agent in common use.¹ However, the B_2O_3 has a greater wetting ability for a ceramic-base material than does the alloy, so a successful braze would not occur.

Some liquid metals will dissolve significant amounts of oxygen at their melting points. Examples include Fe, Cu, Ni, and Ag. This will provide, in effect, some fluxing action. One suspects that this may account in part for the great usefulness of copper- and silver-base brazing alloys. However, the presence of alloy additions that are strong oxide formers can greatly reduce the oxygen solubility in the liquid melt.

It is well known that the oxide in equilibrium with iron at temperatures approaching its melting point is a liquid that has great fluxing action. The presence of the liquid oxide is of great importance in the forge and torch welding of steels. This molten oxide is also important in the flame cutting of low-alloy carbon steels. With small amounts of such elements as Si, Al, and other strong oxide formers, the oxide is no longer

molten and such welding and cutting operations now require a flux. Copper is somewhat similar to iron, although the oxide melts somewhat above the melting point of copper. One nevertheless wonders whether a molten copper-rich oxide may under some conditions be a mild fluxing agent for some copper-base brazing alloys.

The solubility of carbon in nickel is considerably greater than in copper, so one might be able to control the carbon content by varying the copper-to-nickel ratio and saturating the alloy with carbon. When carbon precipitates from nickel or from a copper-nickel alloy it comes out as graphite, which is undesirable.² One wants to have a carbide former in the alloy, Cr and Ti presumably being preferred to Al and Si.

Because Si, Al, and Ti form different oxides they may all be present simultaneously, the degree of reducing conditions required being determined by the component oxide most difficult to reduce. Because Al_2O_3 and Cr_2O_3 are mutually soluble the tendency to form this oxide mixture is somewhat greater.

Figure 7 shows two ways in which some solubility of oxygen in the braze metal is important. In the first case, the oxide film that forms

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Fig. 7. *Left:* If the molten braze metal dissolves some oxygen, then oxygen can be transported through the melt so that an oxide trapped underneath the melt can be reduced. *Right:* As the molten metal enters the joint a small amount of oxide could impede further penetration.

on heating before melting is trapped between the molten metal and the substrate and cannot be reduced effectively except possibly around the edges. Thus, if there is some oxygen solubility the oxide can dissolve, and CO then forms at the free metal surface to bring about the deoxidation. In the second case, as the braze metal flows into the joint some oxygen can be picked up and prevent further penetration. Again, some oxygen solubility helps to solve this problem.

It is not immediately apparent what levels of oxygen solubility are desired, nor is it a particularly simple task to predict how the additions of the active elements will modify the solubility. There is one point, however, about which one can be quite specific. One wants the alloy to be as free of oxygen (or oxide particles) initially as is feasible because any oxygen present will limit the ability of the molten metal to dissolve oxides until the alloy itself has been deoxidized. This is an additional reason why one would want to melt and cast the brazing alloys under vacuum in a graphite crucible.

One can replace nickel with iron or cobalt without much modification of the thermodynamics. However, using Cu-Fe-Ni or Cu-Co-Ni alloys can lead to a number of complications, the foremost being the limited solubilities in the liquids. Also, some composition ranges will lead to phase decomposition of the solid.

For commercial brazing alloys, only the nickel-base series, BNi-1 through BNi-8, can be expected to have sufficient solubility for carbon to be self-deoxidizing in vacuum brazing. The maximum carbon specification, 0.06 to 0.10 wt. % for the different alloys, is unquestionably high enough to provide useful deoxidation, although a higher level might be advantageous. For those alloys that contain chromium, the carbon will surely exist as a carbide in the solid state, but it is less certain what will happen with higher carbon levels in the chromium-free alloys.

CONCLUSIONS

1. In a Cu-Ni-base alloy system a wide range of activities of Al, Si, Cr, and Ti is possible.

2. The simultaneous presence of several active components does not make the deoxidation requirements more stringent.

3. It is difficult to say whether or not the formation of a new oxide by the reaction of the braze metal with the Al_2O_3 substrate is desirable, but we have calculated the amount of aluminum that must be in the alloy to prevent the formation of a second oxide.

4. Although dry hydrogen can be used to reduce the oxides that will form on such alloys, the use of carbon reduction in a vacuum can be very much more effective. This would be most expediently done by having carbon in the braze filler metal.

5. It appears very desirable that the braze metal have some capacity to dissolve oxygen. The Cu-Ni alloys have considerable capacity, but it is reduced by the presence of Ti, Si, Al, and Sn. The degree of oxygen solubility and the alloy additions that will permit such a value remain to be worked out.

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