Thermodynamics of Air-Operating Flux Cored Electrodes and an Analysis of Weld Toughness

The killing reaction between aluminum and nitrogen in steel weld metal is studied and the influence of the reaction product, AlN, on weld toughness is described

BY H. I. KAPLAN AND D. C. HILL

ABSTRACT. Prevention of porosity in steel weld metal deposited with air-operating, flux cored electrodes can be accomplished by using a "killing-agent" such as aluminum to react with nitrogen dissolved in the weld metal. The advantages of aluminum over other nitride formers are considered. The amount of aluminum needed to prevent porosity is calculated thermodynamically for various dissolved nitrogen levels. Experimental flux cored electrodes containing different aluminum levels are used to verify the thermodynamic model. It is concluded that approximately 1.0 wt% aluminum in the weld deposit is needed to prevent porosity when welding without externally applied shielding.

The production of aluminum nitride in the "killing" reaction causes embrittlement of the weld metal. This is demonstrated by welding under different shielding gas and measuring the Charpy toughness of the resultant weld metal.

Introduction

The thermodynamics of deoxidation of steel and weld metal have been studied extensively in the past. When welds are made in oxygen-containing shielding gas, it is necessary to deoxidize the puddle to prevent CO formation and weld porosity. Manganese and silicon are used as deoxidizers jointly, to promote formation of $MnO \bullet SiO_2$ (Ref. 1). The amounts of manganese and silicon required depend on the weld carbon and dissolved oxygen content. $MnO \bullet SiO_2$ is the desired deoxidation product rather than MnO or SiO_2 alone, because of the low activity of the species as $MnO \bullet SiO_2$ compared to the pure oxides. The manganese and silicon in solution are not deleterious to the mechanical properties of steel (in fact they are often beneficial), and the deoxidation product does not adversely affect the properties unless it is present in excess.

For flux cored arc welding without externally applied shielding, additional problems arise due to the presence of nitrogen in the arc atmosphere. The first part of this paper discusses mechanisms for mitigating the effects of nitrogen on weld soundness and discusses the thermodynamics of the reactions involved.

Sound welds can be obtained reproducibly in the presence of nitrogen. However, the mechanical properties of welds made without externally applied shielding are detrimentally affected by nitrogen, and this must be taken into account in any application. In the second part of this paper, typical mechanical properties will be presented, and the factors affecting the weld embrittlement will be described.

H. I. KAPLAN and D. C. HILL are Senior Research Metallurgist and Group Leader, respectively, Linde Research Department, Union Carbide Corporation, Tarrytown, N.Y. 10591.

Thermodynamics of Air-Operating, Flux Cored (AOFC) Electrodes

Origin of the Problem

When welding is done with AOFC electrodes, nitrogen is introduced into the weld pool. The reaction which occurs is

$$N_2\,(g) = 2\underline{N} \qquad (1)$$

where $\underline{N}$ is a nitrogen atom dissolved in liquid iron. This reaction is quite rapid in the welding arc and nitrogen dissolution in the molten metal occurs quickly during transfer.

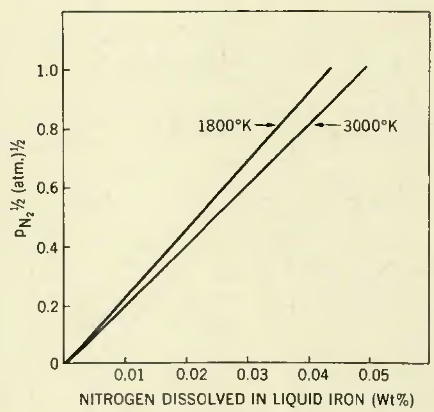


Fig. 1 — The equilibrium solubility of nitrogen in liquid iron

A plot of equilibrium dissolved nitrogen in liquid iron versus $\sqrt{p(N_2)}$ in the atmosphere is shown in Fig. 1. The amount of nitrogen dissolved in liquid iron depends primarily on $\sqrt{p(N_2)}$ and is insensitive to temperature changes. Porosity arises during solidification because of the difference in solubility of nitrogen in liquid and solid iron. The solubility of nitrogen in iron is shown versus temperature in Fig. 2. The solubility limit of nitrogen in liquid iron is about 0.045 wt% (in one atmosphere of nitrogen) while the solubility limit in the solid iron is only 0.012 wt%. As the weld metal begins to solidify, nitrogen is evolved due to the supersaturation of nitrogen in the solidification zone. It is this evolution of nitrogen during solidification which can cause porosity in weldments made when nitrogen is present in the arc atmosphere. Nitrogen gas bubbles are nucleated in the mushy zone during solidification, and are trapped as pores in the finished weld.

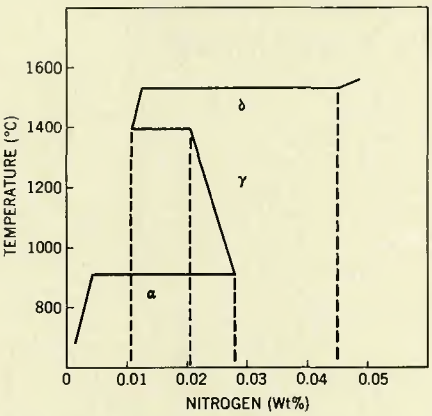


Fig. 2 — Nitrogen solubility in liquid and solid iron versus temperature

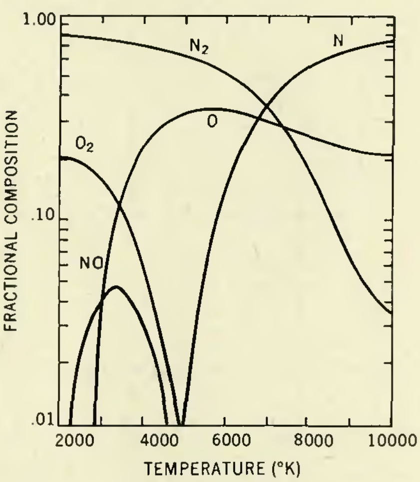


Fig. 3 — Composition of air at one atmosphere versus temperature

The free energy change for the porosity controlling reaction

$$\underline{N}\ (\text{in Fe}) \rightarrow \tfrac{1}{2} N_2\ (g) \qquad (2)$$

can be calculated using thermodynamic data in the literature.* Nitrogen bubbles have a negative free energy of formation during solidification when the dissolved nitrogen content is greater than 0.012 wt% (ignoring surface tension effects). This level of nitrogen is the minimum amount required to cause porosity. (It is possible, however, to have porosity at lower nitrogen levels due to nitrogen segregation during solidification.) This amount of nitrogen will be picked up by arc welding in an atmosphere with a nitrogen partial pressure of 0.55 atm($\sqrt{p(N_2)}$ = 0.74). Air has a nitrogen partial pressure of 0.79 atm ($\sqrt{(p(N_2)}$ = 0.89) and welding in air should result in a total amount of nitrogen in the liquid weld metal of 0.042 wt %. Unless this amount of nitrogen is either excluded from the arc area, gettered or tied up in some manner to prevent nitrogen bubble formation, porosity results.

The nitrogen problem is further aggravated because of the presence of the welding arc. In the arc, the molecules in the air (O_2 and N_2) dissociate to atomic oxygen and nitrogen (Ref. 2). Figure 3 is a plot of the composition of air versus temperature. At arc temperatures there are large amounts of atomic O and N present.

Atomic nitrogen has a higher chemical activity than N_2, and therefore reacts faster and more extensively to dissolve in the iron. As much as 0.12-0.20 wt% nitrogen can be dissolved in the liquid weld puddle during welding because of the presence of atomic nitrogen. This increases the nitrogen problem greatly.

Clearly, unless something is done, it will be impossible to make sound welds in air. We could attempt to prevent the nitrogen from contacting the weld by use of a shield gas — but this is not a solution to the problem. Gas formers could be added to the flux to reduce the partial pressure of nitrogen. However, the nitrogen partial pressure must be reduced below 0.2 before any reduction in nitrogen pickup can be seen. This is shown in Fig. 4, where nitrogen pickup is plotted versus $p(N_2)$. It is difficult to put enough gas formers in an electrode to reduce the $p(N_2)$ to this level, so this presents no easy solution. One can affect the nitrogen pickup by proper control of the welding parameters, as shown in Figs. 5 and 6. Reducing arc voltage and increasing arc current tend to decrease nitrogen pickup, as shown. Regardless of these results, we can see that the best one can do is to reduce the nitrogen pickup; we cannot eliminate it, so the question is — how do we prevent porosity?

Solution of the Porosity Problem

One practical alternative is to prevent nitrogen evolution by forcing its reaction with a nitride former, and thus preventing nitrogen bubble nucleation. The nitride former should be soluble in steel, and form a stable nitride during solidification. The nitrogen partitions into the liquid readily, and the nitride former should partition similarly. The nitride former should not, by itself, be too deleterious to the properties of the steel, and should also be relatively inexpensive. There are several candidates which fit these requirements somewhat. One practical choice appears to be aluminum. The next question is — how much aluminum is required to prevent porosity?

Experiments were done to attempt to measure this value. Welds were made with flux cored electrodes containing various amounts of alu-

All thermodynamic calculations in this report are based on pure Fe-N or Fe-Al-N materials. The effect of the other species in the weld metal (i.e., C, Mn, Si) on the activity coefficient of nitrogen are small for the composition ranges of these species and have therefore been ignored.

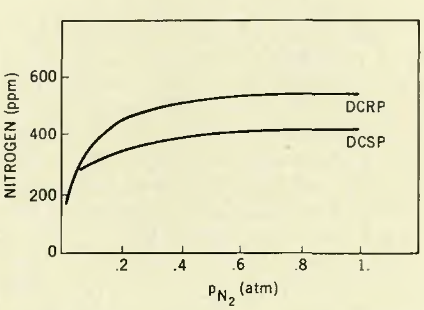


Fig. 4 — Weld nitrogen content versus nitrogen partial pressure

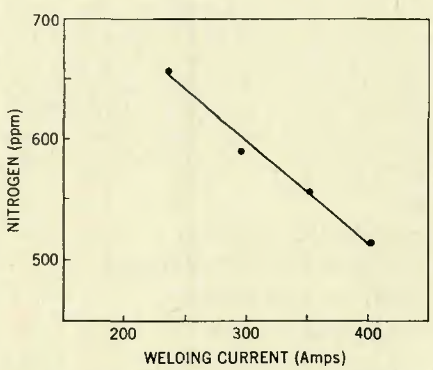


Fig. 5 — Nitrogen content as a function of welding current for multipass welds

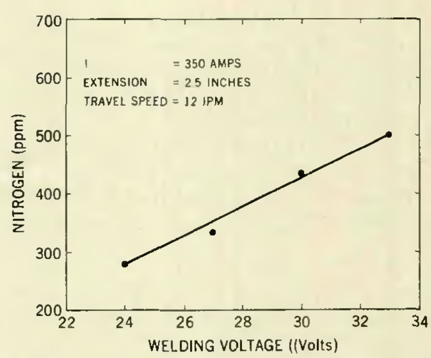


Fig. 6 — Nitrogen content as a function of welding voltage for multipass welds

minum. These electrodes were welded in various nitrogen-containing atmospheres. The welding parameters are shown in Table 1. The welds were cross-sectioned and examined for porosity. A schematic of the results is shown in Fig. 7, a plot of $\sqrt{p(N_2)}$ versus weld aluminum level. The graph is divided into porous and nonporous welds. For each nitrogen content in the shield gas, a minimum aluminum level in the weld is required to prevent porosity. For welding in air, ($p(N_2) = 0.8$), approximately 0.9-1.0 wt% aluminum is required for sound welds.

Thermodynamics of the Aluminum-Nitrogen Equilibrium

The reaction which occurs during solidification to prevent porosity is

$$\underline{Al} + \underline{N} \rightarrow AlN(s) \quad (3)$$

where $\underline{Al}$ and $\underline{N}$ are aluminum and nitrogen dissolved in iron and AlN(s) is solid aluminum nitride.

This equilibrium between Al and N in liquid iron has been studied by various workers (Refs. 3, 4). There is an equilibrium between the aluminum and nitrogen at any temperature such that

$$[Al] \times [N] = K \quad (4)$$

where [Al] and [N] are the concentrations of aluminum and nitrogen and K is an equilibrium constant at any temperature which is determined by the standard free energy change for reaction (3). The value of K can be calculated from the work in the literature (Refs. 3, 4) and is tabulated in Table 2 for both liquid and solid iron. If the product [Al] [N] is greater than K, reaction (3) will go to the right; and it is favorable for AlN to form, thus removing nitrogen from solution in the iron, and inhibiting the tendency for porosity. If one selects an aluminum level, one can calculate the nitrogen content in equilibrium with it as a function of temperature. The nitrogen levels in equilibrium with four selected aluminum levels are also listed in Table 2.

If more nitrogen is dissolved during welding than that in equilibrium with the aluminum in the weldment, AlN forms and nitrogen is removed from solution until the equilibrium in equation (3) is established. If the aluminum level in the weld is high enough, (i.e., see the last two columns in Table 2), the nitrogen level can be lowered by the aluminum nitride reaction below the limit for porosity of 0.012 wt% mentioned previously.

These thermodynamic relationships are shown graphically in Fig. 8. Two horizontal lines are drawn in this figure. The upper horizontal line represents the amount of nitrogen which dissolves in the liquid iron during welding in air. The lower horizontal line shows the amount of nitrogen soluble in solid iron at the melting point. The difference represents the amount of nitrogen which can evolve as nitrogen bubbles during solidification and cause porosity. (Note that because of atomic nitrogen in the arc more nitrogen is actually available for causing porosity.)

The data lines represent the nitrogen content in equilibrium with a fixed amount of aluminum in solution in the weld metal. The two top lines are data for liquid iron, and the four bottom lines are for solid iron. For a particular aluminum level, if the dissolved nitrogen level is above the equilibrium line, AlN forms and nitrogen is tied up in that state. Porosity can be prevented only if the final nitrogen level is reduced below the solubility limit. Aluminum nitride is only stable in liquid iron at very high levels of aluminum and nitrogen and, therefore, does not form to any significant extent until solidification begins. In solid iron, however, AlN is quite stable; and as solidification occurs, AlN forms, tying up nitrogen and suppressing porosity.

Aluminum nitride forms at the solidification front during cooling. For lower aluminum levels, 0, 0.25, and 0.54 wt%, some nitrogen is removed to form AlN. However, the equilibrium nitrogen level for these aluminum levels is still high enough to cause porosity when these electrodes are welded in air. These results are shown in Figs. 9, 10, and 11. At higher aluminum levels, the AlN reaction is more extensive. Aluminum nitride is thermodynamically and kinetically favored over nitrogen bubble formation as evidenced by the lack of significant porosity in welds, which contained 0.94 and 1.39% aluminum (Figs. 12 and 13).

During solidification both reactions

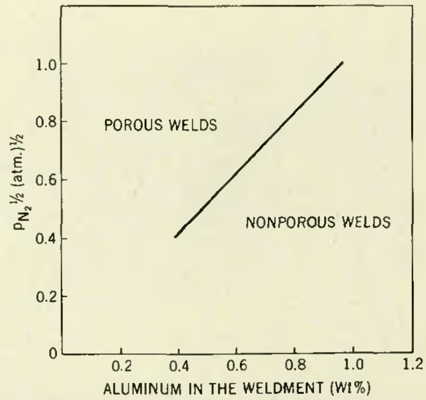


Fig. 7 — Variations in porosity in oxygen-nitrogen atmospheres

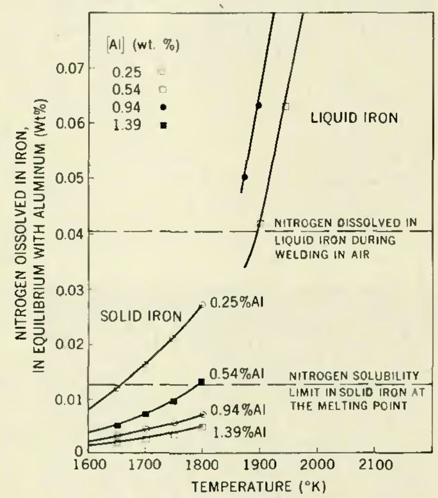


Fig. 8 — Graphical solution of the aluminum-nitrogen equilibrium in iron

Table 1 — Welding Parameters

Voltage	28 ± 1 V
Current	365 ± 25 A
Stickout	1.5 in.
Travel speed	15 ipm
Gas flow (when used)	60-100 cfh total

Table 2 — Equilibrium Constants[a] and Calculated Levels of Nitrogen in Equilibrium with Four Measured Levels of Aluminum at Temperatures Shown

Temp., K	Equilib. const., K[a]	Weight % N for Al levels of: 0.25	0.54	0.94	1.39
	Solid Iron[b]				
1600	2.11×10^{-3}	0.008	0.004	0.002	0.0015
1650	2.92×10^{-3}	0.012	0.005	0.003	0.0021
1700	3.95×10^{-3}	0.016	0.007	0.004	0.003
1750	5.26×10^{-3}	0.021	0.010	0.0056	0.0037
1800	6.91×10^{-3}	0.027	0.013	0.007	0.0049
	Liquid Iron[c]				
1875	0.0475	0.19	0.088	0.050	0.034
1900	0.059	0.236	0.109	0.063	0.042
1950	0.088	0.352	0.163	0.094	0.063
2000	0.129	0.516	0.239	0.137	0.092

(a) Equilibrium constant K = [Al][N]
(b) Reference 2
(c) Reference 3

Fig. 9 — Cross-section of weld made in static air (< .05% Al in weld)

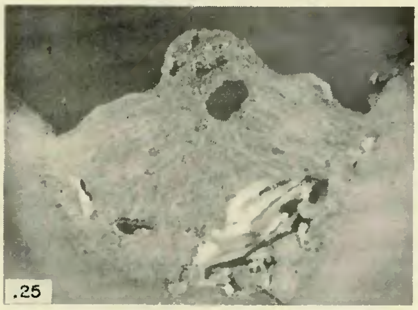


Fig. 10 — Cross-section of weld made in static air (0.25% Al in weld)

Fig. 11 — Cross-section of weld made in static air (0.54% Al in weld)

Fig. 12 — Cross-section of weld made in static air (0.94% Al in weld)

Fig. 13 — Cross-section of weld made in static air (1.39% Al in weld)

(2) and (3) have negative free energy changes as shown in Fig. 14. For aluminum levels in the weld below 0.50 wt%, only small amounts of AlN form and porosity occurs. At much higher aluminum levels AlN formation is favored and sound welds are obtained. At intermediate aluminum levels both reactions may occur, and porosity is dependent on local fluctuations in composition of the weldment. Thus, it is common practice to "overkill" by adding an excess of aluminum.

Measured values of nitrogen by vacuum fusion, which includes both free nitrogen and aluminum nitride, indicate total retained nitrogen contents of air operated weldments of about 0.07 to 0.09 wt%. This indicates the enhanced solubility of nitrogen in liquid iron due to the presence of atomic nitrogen in the welding arc (Ref. 2). Aluminum must be present in sufficient quantity to tie up this excess nitrogen in order to prevent porosity.

The thermodynamic calculations presented verify that aluminum can be used to prevent porosity because aluminum nitride is much more stable in solid iron than in the liquid, and nitride formation occurs when needed most, at the weld solidification front, at the same point where nitrogen porosity can form. There are also kinetic factors involved. Nitrogen segregates during freezing (the nitrogen solubility ratio of liquid to solid is about 4:1) and the nitrogen content in the last liquid to freeze may be quite high. Aluminum segregates in a similar manner and is, therefore, very effective in reacting with nitrogen in the last weld metal to freeze.

Analysis of Factors Affecting Weld Toughness

Mechanical Property Data

Standard AWS multipass welds were made in various atmospheres with several air-operating, flux-cored electrodes to study the effects of weld chemistry and heat input on weld properties.

Standard full size Charpy specimens and 0.252 in. tensile specimens were machined from each weld. Testing was conducted at room temperature. Results of these tests are given in Table 3. Chemistry for each weldment was determined. This data is presented in Table 4.

In addition, the full temperature transition curve was obtained for two of the weldments. These results are plotted in Fig. 15.

The room temperature notch toughness of the weldments was correlated with process and chemistry variables using stepwise multiple regression analysis. The first correlation was made using the composition of the welding atmosphere, the filler metal composition, and the heat input as independent variables. A 98.7% correlation coefficient was measured:

$$\begin{aligned} \mathrm{CVN(RT)} = {} & 129.0 - 61.9\ p(N_2) \\ & + 28.1\ p(O_2) \\ & - 10.7\ \mathrm{wt\%\ Al\ (wire)} \\ & - .758\ \mathrm{heat\ input\ (kJ/in.)} \end{aligned} \quad (5)$$

Table 3 — Mechanical Test Data

Wire	Weld	Atmosphere	kJ/in.	YS	UTS	CVN (RT)
1	A	Air	28.9	69.5	79.1	34
1	B	Air	45.1	65.3	74.3	26
1	C	Air	55.5	64.0	74.9	20
1	D	O_2-Ar	46.6	66.7	75.2	76
1	E	N_2-Ar	44.1	66.9	75.2	21
2	F	O_2-Ar	44.0	69.0	71.4	80
2	G	N_2-Ar	60.0	64.9	68.5	8
3	H	O_2-Ar	45.1	68.3	72.3	85
3	I	N_2-Ar	44.2	67.0	70.7	36

Table 4 — Weld Metal Chemistry for Welds Shown in Table 3

	A	B	C	D	E	F	G	H	I
C	.18	.19	.19	.17	.19	.07	.07	.08	.08
S	.007	.008	.007	.008	.007	.006	.004	.009	.003
P	.006	.005	.005	.008	.007	.009	.007	.009	.010
Mn	.92	.90	.88	.68	.78	1.07	.96	.85	1.05
Si	.09	.09	.10	.10	.10	.30	.25	.35	.30
Al	1.25	1.36	1.34	1.00	1.40	.90	1.30	.60	.90
O (ppm)	145	140	150	345	155	358	130	363	166
N[a] (ppm)	750	760	760	120	770	130	840	130	730

(a) Nitrogen content includes nitrogen contained as aluminum nitride.

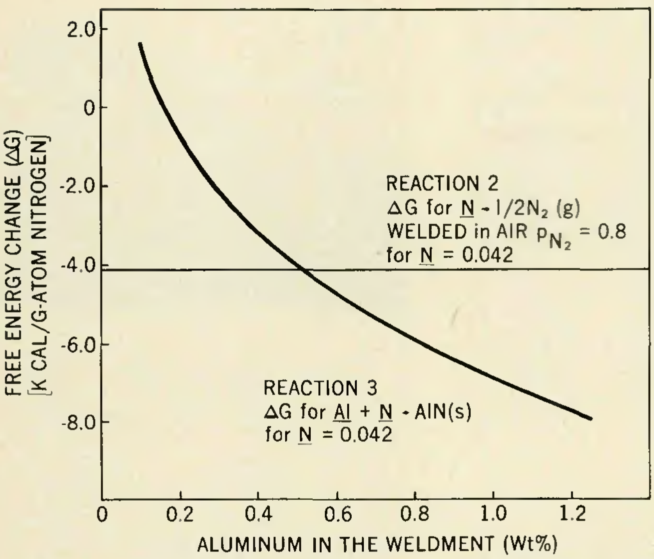


Fig. 14 — Comparison of free energy changes for reactions which can occur during solidification of weldments fabricated using fluorspar aluminum AOFC electrodes

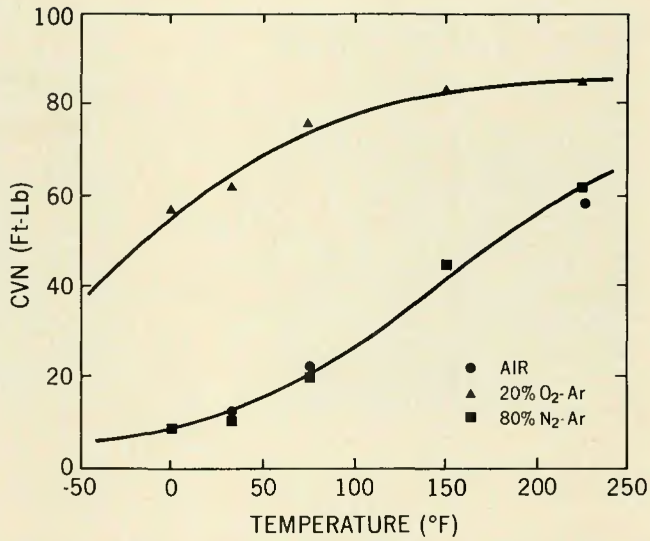


Fig. 15 — CVN toughness versus temperature for various welding atmospheres

Another correlation was made using the resultant weld metal chemistry, and the heat input as independent variables. A 99.8% correlation coefficient was measured:

$$\begin{aligned} CVN(RT) = {} & 130.5 - .073\ \underline{N}\ (\text{ppm}) \\ & - 20.6\ \text{wt\% Al (weld)} \\ & - .523\ \text{heat input (kJ/in.)} \end{aligned} \tag{6}$$

The addition of other chemistry or process variables to these expressions does not improve the correlation coefficient significantly.

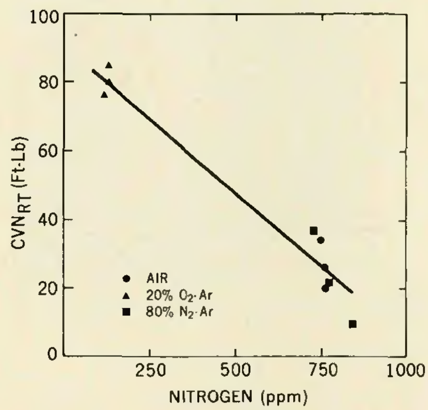


Fig. 16 — CVN room temperature toughness versus weldment nitrogen

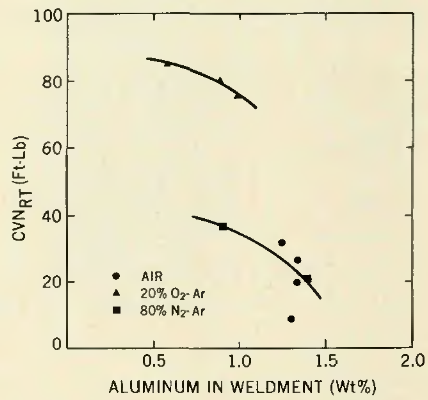


Fig. 17 — CVN room temperature toughness versus weldment aluminum

Discussion of Mechanical Property Results

The presence of nitrogen in weld metal deposited by the AOFC electrodes containing more than 0.50 wt% aluminum is detrimental to notch toughness. This observation agrees with previous work (Refs. 4, 5) which identifies aluminum nitride as a cause of embrittlement in steel. There are several points to confirm the view that the nitrogen is contained predominantly as aluminum nitride:

1. In order to avoid porosity in the solidified weld deposit, the free nitrogen content of the weld metal must be less than the solubility limit of free nitrogen in ferrite at the solidification temperature. This content is 0.012 wt%. No significant porosity was observed in these multipass welds.

2. Free nitrogen in solid steel above 50 ppm substantially increases the strength of the steel through a dislocation locking process. No appreciable increase in the strength of the weld metal is observed in these experiments regardless of the total nitrogen content. In addition, the strength levels observed are consistent with low free nitrogen contents.

Figure 16 shows the behavior of the notch toughness of the weld metal with its total nitrogen content. Figure 15 showed that the presence of nitrogen in the welding atmosphere raises the ductile to brittle transition temperature. As a consequence, the weld metal is less tough at room temperature when aluminum nitride is present in any appreciable amount.

The next most significant chemistry variable is the residual aluminum content of the weld deposit. Figure 17 presents the effect of residual aluminum on toughness. It is noted that the data falls into two ranges depending on whether or not nitrogen is present in the welding atmosphere. If nitrogen is present, aluminum has a more serious effect on toughness because of its interaction with nitrogen than it does when nitrogen is absent. In the latter case, nevertheless, aluminum still has a detrimental effect on notch toughness.

Metallographic studies of these effects are shown in Fig. 18. Figures 18 A, B, and C are welds H, I and F in Table 4 respectively. No significant structural change is observed to occur in these welds despite the wide range of aluminum and nitrogen content. Figure 18D, however, (weld G in Table 4) contains both high aluminum and nitrogen contents. Its structure is quite coarsened and, this combined with its high level of AlN precipitate leads to the low energy brittle fracture, which has been previously reported in the literatu... tem (Ref. 5).

Process variable... toughness. The d... high heat ... welding ... time. S... this s... reas... de...

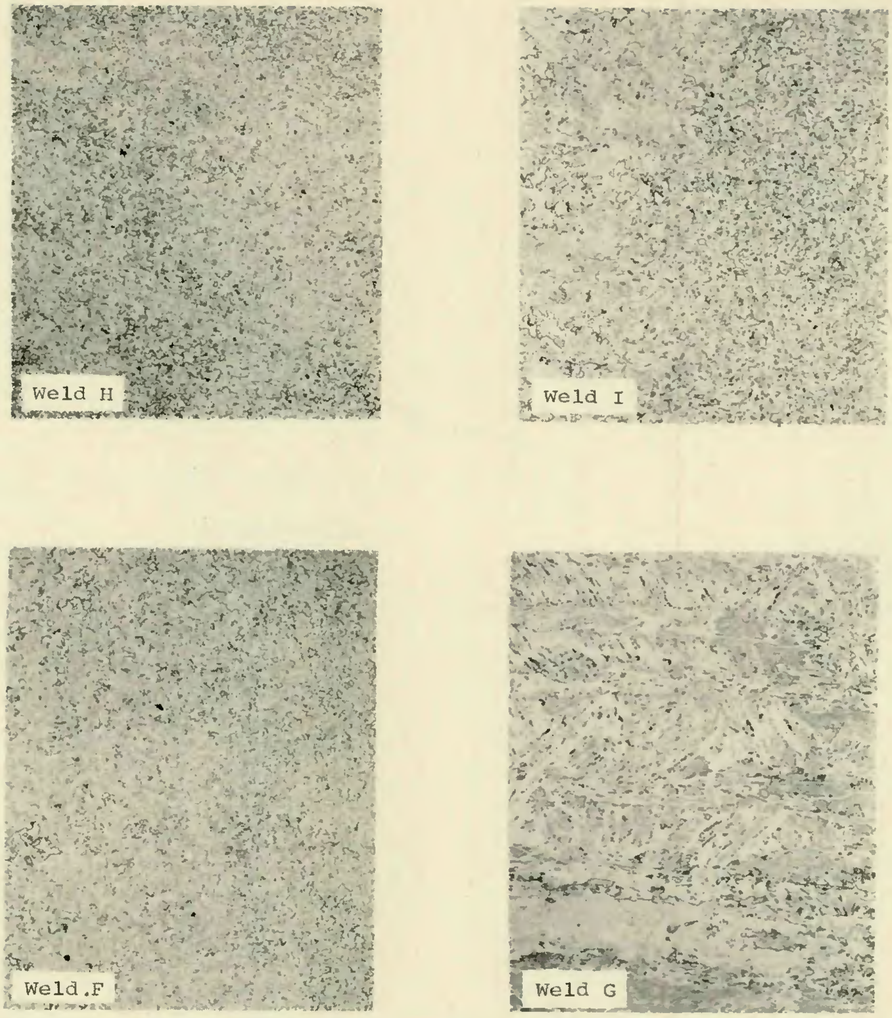


Fig. 18 — Micrographs of welds H, I, F and G (see Tables 3 and 4). X100, reduced

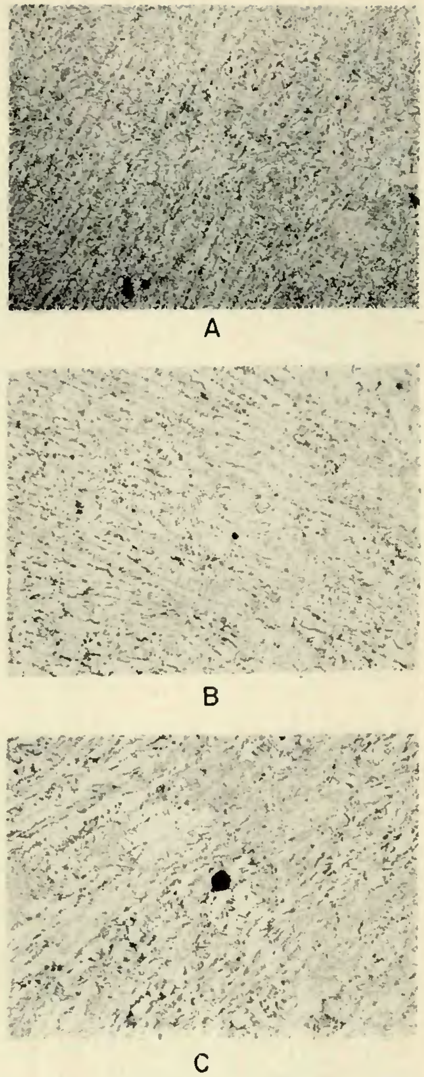
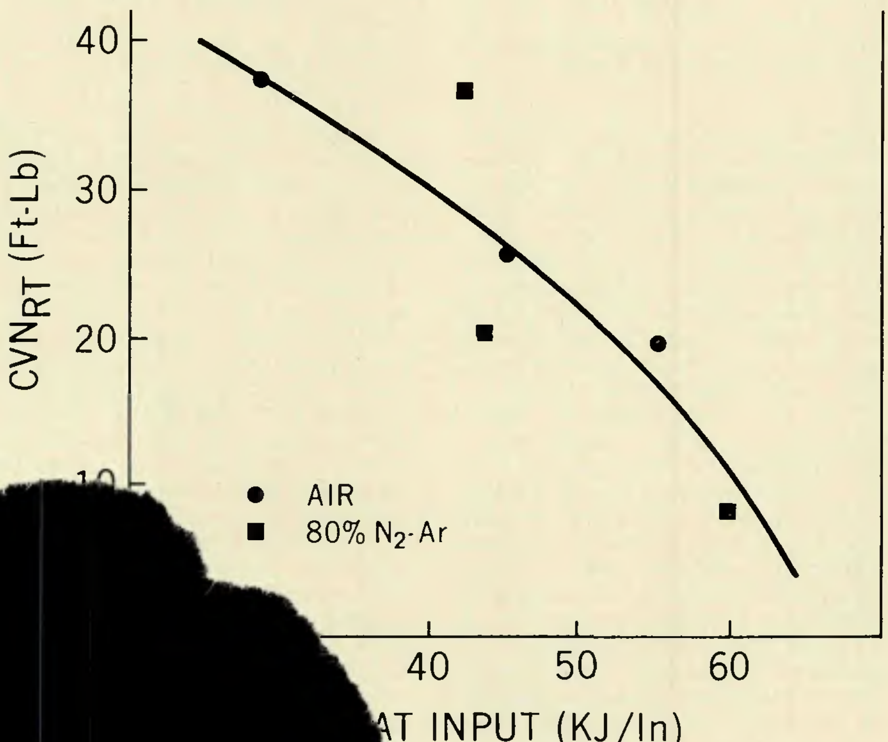


Fig. 20 — Micrographs of welds at increasing heat input: A at 28kJ/in.; B at 45 kJ/in.; C at 55 kJ/in.



ness versus heat input

of solidification time and interdendritic spacing is well known (Ref. 6). As heat input increases, a coarser substructure results. Since notch toughness is inversely proportional to the square root of the substructure size, high heat inputs produce less tough weldments.

2. The longer that the weld puddle remains liquid, the greater is the nitrogen contamination from the atmosphere. (Compare welds E and G, Table 4).

Figure 19 shows the effect of heat input on notch toughness, and Fig. 20 shows micrographs of welds with varying heat inputs. The higher heat inputs led to longer solidification times and coarser structures.

This analysis does not suggest that other chemistry or procėss variables, such as the sulfur or carbon content of the weldment, do not affect notch toughness. The effect of such variables on toughness is well known. This analysis does indicate that for these experiments the variation in toughness observed could be accounted for using the variables discussed.

Summary and Conclusions

Porosity occurs in weldments made by air-operated flux cored electrodes due to evolution of nitrogen during solidification, if insufficient aluminum is present. Nitrogen is dissolved in the weld metal during the welding process, and is evolved during solidification because of the low solubility of nitrogen in solid iron relative to liquid iron. Aluminum prevents this porosity by preferentially reacting with the nitrogen to form aluminum nitride at the solidification front and thus prevent nitrogen bubble formation. A minimum level of aluminum of about 0.8-1.0 wt% in the weldment is required to prevent porosity, but more aluminum must be added to prevent porosity caused by local fluctuations in aluminum and nitrogen contents.

Aluminum is the most desirable metal for prevention of porosity for the following reasons:

1. AlN does not form in liquid iron, but is very stable in solid iron. Therefore, the nitride forms at the same time nitrogen bubbles would form and prevents nitrogen bubble evolution by preferentially reacting with nitrogen in solution.
2. Segregation of aluminum occurs in a similar manner to that of nitrogen and centerline porosity does not occur.

It is concluded that the presence of nitrogen as aluminum nitride is the main source of weld embrittlement. High levels of aluminum in solid solution also degrades toughness in this system as does high heat inputs. Thus, although aluminum can be successfully used to counteract the nitrogen porosity problem, the poor toughness of the welds obtained must be considered in their application.

References

1. *The Making, Shaping, Treating of Steel,* U.S. Steel Corporation, 8th Edition, 1964, p 293.
2. Fast, J. D., *Philips Tech. Rev.*, Vol. 10, 1948, p 26.
3. Evans, D. B., and Pehlke, R. D., *Trans. Met. Soc. AIME,* Vol. 230, 1964, p 1651.
4. Sidey, M. P., *Iron and Steel,* 1967, p 168.
5. Woodfine, B. C., and Quarrell, A. G., *JISI,* Vol. 195, 1969, p 409.
6. Bauer, T. F., Brody, H. D. and Flemings, M. C., *Trans. Met. Soc. AIME,* Vol. 235, 1966, p 646.