Diffusion Welding of Reactive and Refractory Metals to Stainless Steel

Use of the proper filler metal permits the joining of Types 430 and 321 stainless steel to titanium, tantalum and other refractory base metals

BY R. LISON AND J. F. STELZER

Introduction

The utilization of costly metals and alloys is increasing. As a result, there is a demand for methods to join these expensive metals with the more commonly used metals. This requirement is not always caused by cost, but also by the desire for new, basically improved structures.

A precondition for the utilization of the advantageous properties of dissimilar metals within one structure is the generation of transition joints which fulfill proposed requirements; these include a long lifetime at high temperatures for gas turbines or neutron compatibility and corrosion resistance in nuclear technology. Joining dissimilar metals enables us to use the most suited material for each part of the structure.

There is a growing demand also for suitable joining methods, because of the increasing variety of metals and their improved properties. There are cases where a mechanical construction suffices, but frequently welding is inevitable. Each welding process raises specific problems.

Welding Dissimilar Metals

In the case of fusion welding, the structure and properties of the base metals are changed. Even if similar metals are fusion welded, a deviation of the optimum parameters causes a deterioration of the properties of the joint. In the case of dissimilar metals, welding parameter compromises are necessary; these mostly are unfavorable to the transition zone.

When using fusion welding, the generation of an alloy of the base metals cannot be suppressed in the region of melting. If metallurgical incompatibility occurs, either suitable interlayers or specially alloyed filler metals are employed. Thus, a composition of the joint with acceptable properties is accomplished.

Well suited for this purpose are the gas tungsten arc process and, even better, electron beam welding. Here the possibility is given for the precise regulation of both the weld energy level and beam location; this permits close control of the weld shape and the ratio of the two base metals in the weld metal. The high energy density enables narrow welds. Therefore, it is possible to insert one or more interlayers without the need for much space.

Solid State Welding

The group of processes that constitute solid state welding is even better suited to the joining of dissimilar metals, because no alloy is generated in the liquid state.

Diffusion Welding

This process offers the advantage of precisely dimensioned interlayers (filler metals) and the formation of very thin intermetallic layers between the dissimilar base metals. This leads to the most important theme in the context of diffusion welding.

The parameters during the fabrication of such a joint change the properties of the base metals. Often compromises are necessary and a certain deterioration of the properties of the transition zone must be accepted. This zone is a narrow layer of an alloy generated by the movement of atoms at the interface through the heated but still solid metal. The vicinity of this zone is also subjected to residual stress during cooling, which is determined by the thermal expansion properties and Young's moduli.

Due to this, and also metallurgical reasons, not every random pair of metals delivers a satisfactory joint. Therefore, the use of one or several intermediate metals is advisable. The thermal coefficients of expansion of these filler metals and of the base metals should have a uniform change from one base metal to the other. These filler metals should have good mutual solubility, but the occurrence of intermetallic phases should be suppressed as far as possible.

Although the generated diffusion zone is not required for the completion of a joint, it can scarcely be avoided. Compared to fusion welding, diffusion welding offers the advantage of limiting the thickness of the transition zone according to the time and temperature of welding. Thus, it is possible to avoid concentrations.
which exceed the solubility and often exhibit the formation of intermetallic phases.

The above topics were the subject of experimental and theoretical research.

**Diffusion Welding Research**

Experiments were performed concerning the diffusion welding of metals of the groups IVA (Ti, Zr), Va (Cb, Ta, V) and Vla (Mo) with AISI Types 430 and 321 stainless steel. The physical properties of the dissimilar base metals are very different, e.g., the melting point range is as high as 1000°C (1832°F). We found that the following classification of the joints is appropriate: a—directly weldable metals; b—joints with one or more filler metals, b1—producing in one operation, and b2—producing in two or more operations.

To the first group belong pairs of metals which yield a metallurgically satisfactory joint produced at a given temperature where the residual stresses remain tolerable.

The second group includes base metals with very different chemical and physical properties. Here one or more filler metals are necessary. Case b2 occurs when the welding temperature for joining one base metal to the adjacent filler metal exceeds the melting point of the other base metal or one of the remaining filler metals. Also belonging to case b2 are joints with filler metals deposited by electrolytic or vapor deposition methods.

Figure 1 shows ranges of temperatures recommended by Kasokov for the welding of some metals. Wide overlapping, as in the cases of Ti-Zr or Ta-Cb, points to favorable conditions for the welding of these combinations. Yet metallurgical compatibility must also be present, since joint strength largely depends on this factor.

The diffusion zone shows optimum properties if a combination forms a complete series of solid solutions, e.g., Cu-Ni, Ag-Au, Mo-Ti, V-Cb. The joining of these combinations is relatively easy to control, since the thickness of the diffusion zone does not have an appreciable influence on the mechanical properties.

The properties become less favorable if intermetallic phases occur, as in binary alloys with limited solubility, e.g., Ti-Fe, Zr-Fe, Al-Fe. In some cases (e.g., Al-Fe), it is possible to succeed in obtaining a useful joint by applying precise control and appropriate joining geometry. There are still other structures within the transition zone, whose properties lie between those of solid solutions and intermetallic phases.

Before starting experimental work it was important to obtain information about the expected properties in the transition zone. Criteria were found in the literature.

**Compatibility of Base Metals and Choice of Suitable Filler Metals**

In the periodic system of elements, those with similar properties are in the same column and are designated as groups numbered from I to VIII. Figures 2 and 3 show the thermal expansion coefficients and the melting points of the metals in the groups. It can be seen that Fe, contained in many alloys, and the metals of groups IVA, Va and Vla differ widely in these properties. They do not match the requirements for direct welding. For the choice of the filler metal, two well known approximation equations are given. For metals with cubic lattice:

$$T_\alpha \approx 0.02$$

where

$$T_\alpha = \text{melting point in } ^\circ K;$$

$$\alpha = \text{thermal expansion coefficient}.$$

From this follows that for a pair of metals:

$$\frac{T_\alpha}{T_\beta} \approx \frac{\alpha_1}{\alpha_2}$$

If the thermal expansion coefficient of a filler metal lies between that of the base metals, the melting point of the filler metal should also lie between those of the base metals. This is valid for metals with a cubic lattice but not for those of group Vla with a hexagonal lattice.

The second equation is:

$$\alpha \approx \frac{k}{R_a E}$$

where

$$k = \text{Boltzmann's constant; }$$

$$R_a = \text{interatomic distance at equilibrium; }$$

$$E = \text{Young's modulus}.$$

The second equation shows that metals with a small thermal expansion coefficient have a large Young's modulus. If they are joined to a metal with a high thermal expansion coefficient, considerable residual stress is developed. This concerns principally combinations with Mo or W. The criteria shown in the literature for the formation of binary systems indicate, when compared to Figs. 2 and 3, that the elements forming solid solutions

![Fig. 1—Temperature ranges recommended for diffusion brazing](image-url)
Fig. 2—Mean linear expansion coefficient of the metals within the periodic system

Fig. 3—Melting temperatures of metals within the periodic system

Fig. 4—Mutual effects of Ti with the elements of the periodic system

Fig. 5—Mutual effects of Fe with the elements of the periodic system
with another element are to be found in the same group or an adjacent group of the periodic system. These metals do not differ much in their melting points or thermal expansion coefficients.

**Joints Between Stainless Steel (AISI Types 321 or 430) and Metals of Group IVa**

Stainless Steel with Titanium. This joint may serve as representative of this joint family. The solubility of Fe in \( \alpha \)-Ti lies between 0.05 and 0.1 wt-%. If the Fe content increases, the intermetallic phases TiFe and TiFe\(_2\) form; this causes a change of the mechanical properties. A Ti-Fe alloy with 0.14 wt-% Fe has a hardness of 199 VHN and tensile elongation of 18.5%. At 2.5 wt-% Fe, the hardness increases to 450 VHN and elongation decreases to 2.5%. This is a disadvantageous condition for a direct joint and is made worse by a ratio of 2 for the thermal expansion coefficients.

In our experiments, it was basically possible to join pure Ti with AISI Type 321 stainless steel directly. But when preparing the specimens for tensile testing, seven of eight specimens broke. The intact specimen showed a tensile strength of 28 MPa (4.01 ksi). The brittle behavior of this combination indicates a need for intermediate metals.

**Suitable Filler Metals.** The mutual effects of Ti with other elements are given in Fig. 4.\(^{10}\) The two modifications, hexagonal \( \alpha \)-Ti and cubic \( \beta \)-Ti, display different alloying characteristics.

The \( \beta \)-Ti forms a complete range of solid solutions with the elements V, Cb, and Ta, whereas the behavior of \( \alpha \)-Ti is more limited in this respect. At 700°C (1292°F), 3 wt-% V can be dissolved in \( \alpha \)-Ti. Vanadium dissolves 87 wt-% Ti at this temperature. These promising properties are further enhanced by thermal expansion coefficients which form a ratio (Ti:V) of 8.5:8.3. Thus, V seems to be a suitable filler metal.

The compatibility of V with the other base metal—AISI Type 321 stainless steel—is now considered. Vanadium forms only with \( \alpha \)-Fe a complete series of solid solutions. In gamma-Fe its solubility is limited, (Fig. 5), and intermetallic phases are present. With regard to the alloying elements in stainless steel, only Cr is of unlimited solubility in V, whereas Ni has only a limited solubility. In the solid state the phases VNi\(_{12}\), VNi, and V\(_3\)Ni are found.\(^{10}\) Although the carbon content of the given steel is low, there exists the possibility of diffusion into the V. In this case vanadium carbides would appear. We learned in a series of experiments that it is apparently not possible to obtain useful joints between V and AISI Type 321 stainless steel. Additional filler metals are necessary.

From the literature,\(^{2}\) some useful filler metals for the combination V-Fe are known. Besides copper bronze, preproduced sheets of three-layer V-Ni-Cu are recommended. In our experiments, in addition to the V-Ni-Cu, a sheet of three-layer V-Cu-Ni was inserted because of the better order of the thermal expansion coefficients. Also, from the metallurgical point of view, the latter series offers an advantage in that V has only a limited solubility for Ni; if this solubility is exceeded, the phases VNi\(_{12}\), VNi, and V\(_3\)Ni form. Copper also has only a...
Fig. 7—Diffusion braze between Ti and AISI 430 via filler metals.

Fig. 8—Diffusion braze between Zr2Sn (Zircaloy 2) and AISI 321 via filler metals.
limited solubility in V but the system remains free of intermetallic phases.

Nickel and Cu form an uninterrupted series of solid solutions. The segregation of a NiCu phase in the solid state is controversial.\textsuperscript{10,11} The solubility of Cu in Fe is limited, but intermetallic phases do not appear.

Nickel and gamma-Fe form a complete range of solid solutions. The solubility of Ni in alpha- and delta-Fe is limited, to about 10 atomic-% at 200°C (392°F). A higher Ni content causes a segregation of Fe,Ni, FeNi and FeNi\textsubscript{3} phases.

Preproduced three-layer filler metal sheets, as well as separately intro-
duced metals of the given sequence, were satisfactory for diffusion welding of Ti to ferritic or austenitic stainless steels. Success was also achieved with the application of preproduced two-layer V-80Cu20Ni and V-Ni13Cr7Fe filler metals. Figures 6 and 7 show such combinations.

The filler metals were preproduced from sheets with thicknesses between 1 and 5 mm (0.04 and 0.20 in.) if no foils were available. Later on, foils of 0.1 mm (0.04 in.) thickness were also successfully used.

Stainless Steel with Zr2Sn. This combination is of special interest in nuclear technology. Since Zr also belongs to group IVA, similar properties are to be expected as for Ti. Zirconium in alpha-Fe has a solubility of only 0.35 atomic-%; alpha-Zr at 800 C (1472 F) can dissolve 4 atomic-% Fe.

During solidification, ZrFe, is formed, which converts to Zr,Fe in the solid state. The eutectic existing at the Zr side shows a melting point of 934 C (1713 F). Zirconium cannot dissolve appreciable amounts of the alloying elements Cr and Ni, and vice versa. Zirconium forms intermetallic phases with both elements. The ratio of thermal expansion coefficients Zr/AISI Type 321 stainless steel is 6.5/18; for AISI Type 430 stainless steel it is 6.5/12. Making a direct joint by welding is, therefore, not advisable and filler metals should be used.

Suitable Filler Metals. Again V, being located in a neighboring group, offers limited solubility without intermetallic phases in the solid state. The transition from V to stainless steel has already been described above. The thermal expansion coefficients are to be taken into account.

In the transition zones. But the insertion of an additional metal (Ti) is not favorable for other reasons.

Joints Between Stainless Steel (AISI Type 321 or 430) with Metals of Group IVA

There are three metals in this group: V, Cb and Ta. The transition from V to steel has already been described above and needs no further discussion. The other two metals, Cb and Ta, form with V a complete series of solid solutions, with the system Ta-V segregating TaV, in the solid state. This compound does not have an appreciable influence on the properties of the joint.

The same transition series as described above can be inserted from V to steel. Diffusion welded joints of Va-metals with stainless steel are exhibited in Fig. 9.

Joints Between Stainless Steel (AISI Type 321 or 430) with a Metal of Group IVA

From this group Mo was chosen for examination as the most widely used metal of the group. Its thermal expansion is 30% of that of austenitic steel and 40% of that of ferritic stainless steel. The melting points of the base metals are 1000 C (1800 F) apart.

The binary system Fe-Mo contains limited solubilities and intermetallic phases. Mo dissolves 16.7 Fe at 1480 C (2696 F) and 4.5 atomic-% at 1100 C (2012 F). With further decreases in temperature, the solubility also decreases. On the other hand, the solubility of Mo in Fe amounts to 26 atomic-% at 1450 C (2642 F), but gamma-Fe dissolves only 4 atomic-%. The system Mo-Fe contains the phases MoTa, MoFe and MoFe. From the presented points of view, the welding of Mo directly to an Fe alloy does not appear promising. Filler metals are necessary. Figure 10 exhibits the mutual effects of Mo with the elements of the periodic system. Vanadium, Cb and Ta of group IVA display attractive alloying behavior with Mo.

Unfortunately, welding between Mo and V failed. Apparently the reason is to be sought in the thermal expansion ratio of 5.1/6.3 for Mo/V, which leads to excessive residual stresses during cooling, augmented by the high Young's modulus of Mo.

The next experiments concerned Ta as a filler metal. The ratio of the thermal expansion coefficients is at 5.1/6.5 for Mo/Ta more promising. The further transition to the stainless steel has already been described above. The widely diverging melting points do not allow the production of the joint at one temperature. The transition of Mo-Ta-V-Ni-Cu-AISI 321 was joined in two operations. The first accomplishes

Table 1—Mechanical Properties of the Materials Joined in the Calculation Example

<table>
<thead>
<tr>
<th>Material</th>
<th>Young's modulus, MPa</th>
<th>Thermal expansion coefficient, 1/K</th>
<th>Poisson's ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vanadium</td>
<td>140.000</td>
<td>8.3 x 10^-6</td>
<td>0.34</td>
</tr>
<tr>
<td>Copper</td>
<td>127.000</td>
<td>17.7 x 10^-6</td>
<td>0.34</td>
</tr>
<tr>
<td>AISI 321</td>
<td>175.000</td>
<td>18.2 x 10^-6</td>
<td>0.3</td>
</tr>
</tbody>
</table>
the combination Mo-Ta-V at 1500 °C (2732 °F) in 40 minutes (min). This combination is then joined to stainless steel in a second operation with foils of Ni and Cu at 850 °C in 20 min. To save time, however, two Mo-Ta-V combinations may be placed together with their V surfaces separated by a parting compound; this prevents the joining of the two V-layers. In this way only 1.5 joining operations are necessary for each Mo-Ta-V combination.

The order of the thermal expansion coefficients for the combination of Mo-Ta-V-Ni-Cu-AISI Type 321 stainless steel is 5.1-6.5-6.3-13.3-17.7-18 and shows a desirable uniformity of change from one base metal to the other. Such a joint is shown in Fig. 11.

Mechanical Property Predictions for Dissimilar Metal Joints

Theoretical examinations were conducted to find a method to predict the mechanical behavior of dissimilar metal joints with filler metals. For consideration we chose cylindrically shaped specimens consisting of V and stainless steel (AISI Type 321) diffusion welded with Cu filler metal. This structure was subjected to computer analysis using finite elements. Thus, its residual stress fields and the consequent stored potential energy could be revealed.

We analyzed several cases with different ratios of length to diameter, varying the filler metal thicknesses and the temperature changes.

Model

To form the model, a quarter of the cylinder sufficed because of symmetry. This is subdivided into finite elements as displayed in Fig. 12. In the vicinity of the filler metal, the element dimensions perpendicular to the joint are reduced in order to obtain more detailed information in this area where the stress is concentrated.

The mechanical properties of base metals and the filler metal are listed in Table 1.

Stress Fields

For ease of presentation in this context, we deal with reference stresses, which are put together from the six normal stresses according to the von Mises hypothesis. The reference stress is always positive, concealing the fact that the normal stresses show the positive sign in some regions and the negative sign.

During heating, the metal with the higher thermal expansion coefficient is restrained from normal expansion, thus producing compressive forces with negative stress. The metal with the lower expansion coefficient behaves in the opposite manner.

Results are graphically presented in Figs. 13 and 14. The patterns of reference stresses are plotted vertically over the upper section corresponding to Fig. 12. Both cases refer to a cylinder of 125 mm (4.9 in.) length and 25 mm (1 in.) diameter, but differ in the thickness of the copper filler metal. The thicknesses are 5 and 0.1 mm (0.2 and 0.04 in.) in the cases of Figs. 13 and Fig. 14, respectively. The temperature change is 10 K (10 °C, 18 °F) in both cases.

There is little difference between the two cases in the magnitude and contour of stresses. The maximum stress appears in the V and immediate proximity to the filler metal. Here, if any, a crack would preferentially set in. Characteristic stress valleys occur in the base metal parallel to the filler metal at a short distance from the transition.

<table>
<thead>
<tr>
<th>Case</th>
<th>Steel length, mm</th>
<th>Filler metal thickness, mm</th>
<th>Vanadium length, mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>60</td>
<td>5</td>
<td>60</td>
</tr>
<tr>
<td>2</td>
<td>62.45</td>
<td>0.1</td>
<td>62.45</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Case</th>
<th>Energy in steel, Nmm</th>
<th>Energy in filler metal, Nmm</th>
<th>Energy in vanadium, Nmm</th>
<th>Sum, Nmm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>8.349</td>
<td>0.488</td>
<td>1.42</td>
<td>10.25</td>
</tr>
<tr>
<td>2</td>
<td>8.69</td>
<td>7.8 • 10⁻⁴</td>
<td>1.478</td>
<td>10.16</td>
</tr>
</tbody>
</table>

WELDING RESEARCH SUPPLEMENT | 313-s
stored Potential Energy

The amount of potential energy equals the deformation load on a stressed structure. If it exceeds a certain limit, the structure will fail. The potential energy W is commonly written as:

\[ W = \frac{1}{2} \sigma \delta \varepsilon \mathrm{d}V \]  

(1)

with \( \sigma \) = stress; \( \delta \varepsilon \) = variation of strain; and \( V \) = volume.

In the finite element analysis, the potential energy is treated as:

\[ W = \frac{1}{2} \{u\}^T \{k\} \{u\}, \]  

(2)

where \( \{u\} \) is the displacement vector of the nodes of the net and \( \{k\} \) is the stiffness matrix of the structure.

This value was calculated for each parametrical case. It agrees very well with the results gained by the reduced method of summing each of the individually integrated potential energies of the adjacent metals:

\[ W = \frac{T^2}{2} \Sigma \alpha_i^2 \lambda_i \frac{E_i}{L_i}, \]  

(3)

with \( T \) = temperature change; \( \alpha \) = cross section; \( \alpha_i \) = thermal coefficient of expansion; \( L \) = length of individual pieces; \( E \) = Young's modulus; and \( i \) = numbering index of joint metals.

The temperature change can be treated as a constant, since it is normally uniform over the entire structure in length and cross section. The number of cases increases from three in the case of one filler metal joining two base metals, to five, if three filler metals are used. In the case of the above treated example, equation (3) becomes:

\[ W = \frac{T^2}{2} \left[ \alpha_1^2 \frac{(L-s)}{L} \frac{E_1}{E_i} + \alpha_2^2 \frac{s}{E} + \alpha_3^2 \frac{E}{2} \right] \]  

(4)

where \( s \) = filler metal thickness.

Results

The total potential energy depends only slightly on the filler metal thickness, \( s \), in the special case of Table 2. The considerable decrease of energy in the very thin filler metal of case 2 shows only a slightly reduced total energy content, as compared with case 1. This however, is not generally valid.

In other cases, we found that with a decrease of the filler metal, an increase of the total potential energy took place. Therefore, the decision on an optimum thickness lies in an individual match of the variables in equation 3 for each joint under consideration.

Concerning the “ideal filler metal (rim),” it can be said, from the mechanical point of view, that the filler metal properties should approach as nearly as possible to:

\[ \alpha_i^2 E_i \rightarrow \frac{\alpha_i^2 E_i + \alpha_i^2 E_i}{2} \]  

(5)

where the indices 1 and 2 identify the base metals.

Conclusion

The results of the present investigation show the possibilities of joining stainless steel with the reactive and refractory metals. Because of the diverging physical and metallurgical properties, filler metal must be used.

The laws of metal science serve for the choice of filler metals. To assess the mechanical behavior of the joint and to choose the filler metal thickness, it is worthwhile to calculate the stress distribution by determining the potential energy.

Diffusion welding is well suited for the production of dissimilar metal joints with selected filler metals.

References


WRC Bulletin 245

January 1979

A Fracture-Mechanics Evaluation of Flaws in Pipeline Girth Welds

by R. P. Reed, H. I. McHenry and M. B. Kasen

Fracture-mechanics methods were used to provide a basis for assessing the significance of flaws in girth welds in a buried arctic oil pipeline. The objective was to illustrate the approach based on current knowledge and to define areas where further work will increase the validity of such analyses. Various fracture-mechanics analyses were used to calculate a series of allowable flaw-size curves in accordance with worst case requirements set by the Office of Pipeline Safety Operations (OPSO).

Publication of this bulletin was sponsored by the Weldability Committee of the Welding Research Council. The price of WRC Bulletin 245 is $11.00 per copy. Orders should be sent with payment to the Welding Research Council, 345 East 47th St., New York, NY 10017.