Effect of Nickel Plating on Fe-BCu-Mo and -W

Nickel plating on the Fe in Fe-BCu-Mo and -W restrains the deposit of brittle Fe alloy (at the Mo or W boundary) that causes brazed joint exfoliation

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ABSTRACT. In the Cu brazing of Fe to Mo or W, the dissolution and deposit of base metal takes place; the Fe base metal dissolves into molten Cu filler metal and, simultaneously, the dissolved Fe deposits as plate-like Fe-Mo-Cu or Fe-W-Cu alloy phase from the Mo or W base metal under a constant brazing temperature. Furthermore, Fe of the deposited phase penetrates into the Mo or W base metal so that the intermetallic compound, Fe7Mo6 or Fe7W6, which is inherently brittle, is formed at that base metal boundary. Consequently, a significant loss of mechanical properties of the joint occurs.

Ni plating of 1.1-4.3 μm (0.000044-0.000172 in.) thickness on the Fe base metal to be joined restrains the dissolution and deposit of base metal; it also improves the mechanical properties of both deposited and intermetallic compound phases by alloying Ni. The shear strength of the joint is thereby improved.

Introduction

In recent years, considerable emphasis has been given to Mo and W in various industries (e.g., electric, electronic, aerospace, nuclear, chemical) because of their excellent high temperature properties.

Often, it is desirable to braze Mo or W to Fe for extended use. However, the direct brazing of Mo or W to Fe tends to cause the exfoliation of the joint; this results from the deposit of the brittle Fe alloy phase at the Mo or W base metal boundary (Ref. 1) due to a "dissolution and deposit of base metal" (Ref. 2).

To correct this defect, the Ni plating of 2-3 μm (0.00008-0.00012 in.) thickness on the Fe base metal prior to brazing has been practiced in industry. However, the explanation for the improvement mechanism has not been given.

This paper clarifies the effect of Ni plating on Fe-BCu-Mo and -W joints in terms of the dissolution and deposit of base metal. It also examines the shear strength of the brazed joints.

Experimental Procedure

Tests were performed utilizing both similar and dissimilar joints which adequately combined Fe (99.65% Fe, 0.013% C), 0.11% C steel, Mo (99.9%), W (99.9%) and Ni (99.9%); the joints were subjected to polishing (#1000) and cleaning with acetone.

Pure Cu (99.99%) and Ag (99.99%) were used as filler metals, and W wires of appropriate diameters were adopted in order to space the joint.

Ni plating on the 0.11% C steel to be joined was conducted from Watts bath (240 g/l NiSO4 · 6H2O, 45g/l NiCl2 · 6H2O, 30g/l H3BO3) under stirring at 55°C (131°F), pH 4 and 3 A/dm². Thickness of the Ni layer was measured by using a thickness tester.

All Cu brazing—except for similar Mo and W joints which, because of either the inferior wettability or experimental convenience, were conducted in an Ar atmosphere—was done in a vacuum condition (Ref. 3); 0.133 Pa (10⁻³ torr). Also, all Ag brazing was carried out in an Ar atmosphere.
After brazing, each specimen was cut in a section perpendicular to the brazed surface and then polished for metallographic examination. Also, EPMA analysis to the section was performed under the following conditions: voltage —20 kV; current —3.4 nA. The etchants used were 2% nital and H₂O₂ (35%). In order to check the mechanical property of the brazed joint, each of a series of 0.11%C st.-BCu-Mo and -W joints was submitted to shear tests (Ref. 3) after filing away the fillet.

Results and Discussion

Similar Brazing of Fe, Mo and W

Figure 1 shows cross-sectional micro-structures and EPMA line analyses of similar Fe, Mo and W joints at 50 μm (0.002 in.), brazed with Cu at 1125°C (2057°F) for 8 min. In similar joints, the dissolution of the base metal into molten Cu does not exceed its equilibrium quantity fixed at the brazing temperature, no matter how long the heating time. Also, the base metal boundary is saturated with Cu by the penetration of molten Cu.

Using EPMA quantitative analysis (Ref. 4), Fe that dissolved into molten Cu at brazing temperature in a similar Fe joint was determined to be approximately 3%; this is an amount about equal to the liquidus line of the Fe-Cu phase diagram shown in Fig. 2 (Ref. 5). In similar Mo and W joints, Mo and W quantities in Cu were 0.1% and 0.4% respectively. This experimental evidence means that both Mo and W can be wetted with molten Cu, even though it has been reported that Mo and W are insoluble in liquid Cu (Ref. 6).

For these specimens there is no particularly characteristic microstructure at the base metal-filler metal interface.

Growth of Plate-like Phase in Fe-BCu-Mo and -W

Figures 3 and 4 show the microstructures of Fe-BCu-Mo and -W joints at 50 μm (0.002 in.), brazed at 1125°C (2057°F) for 2, 8 and 32 min. Also, Figures 5 and 6 show EPMA line analyses of the area indicated by the arrows in Figs. 3 and 4, respectively.

Because of the changes in the relative position of the base metal-filler metal interfaces and W spacer, it is apparent in Figs. 3 and 4 that the Fe base metal is eroded by molten Cu; simultaneously, the plate-like phase grows increasingly from the Mo or W base metal with heating time —that is to say, a “dissolution and deposit of base metal” takes place.

From Figs. 5 and 6, it is shown that the plate-like phase consists of Fe-Mo-Cu or Fe-W-Cu alloy; also, small amounts of Mo or W can be recognized in the insular phase of nearby Fe base metal. Further, the other plate-like white phase (hereinafter called “white phase”) can be observed between the plate-like phase and the Mo base metal in Fig. 3 or W base metal in Fig. 4. Observing the W spacer-Mo or W base metal interface reveals that the white phase develops into the Mo or W base metal.

Figure 7 shows the oblique-section microstructure of the plate-like phase in Fe-BCu-Mo joint; the streaks of the plate-like phase, as seen in Fig. 3, are the grain boundaries.

Figure 8 shows x-ray diffraction patterns obtained from the ruptured brazing surface of the Mo and W base metals in 0.11%C st.-BCu-Mo and -W joints. In shear tests, destruction of the joint occurred at the Mo or W base metal boundary as later described in detail. From Fig. 8, it is obvious that Mo, αFe, Cu and intermetallic compound Fe₇Mo₆ phases on the Mo fracture surface, and W, αFe, Cu and intermetallic compound Fe₇W₆ phases on the W fracture surface can be recognized, respectively; this agrees well with the phases existing at the brazing temperature, 1125°C (2057°F) in that these are: γFe, αFe, Fe₇Mo₆, and Mo.
Fig. 4 — Growth of plate-like phase in Fe-BCu-W joints at 50 µm (0.002 in.), brazed at 1125°C (2057°F) for 2, 8 and 32 min. X200 (reduced 42% on reproduction)

Fig. 5 — EPMA line analysis of Fe-BCu-Mo joint, brazed at 1125°C (2057°F) for 2 min, in Fig. 3.

Fig. 6 — (left) EPMA line analysis of Fe-BCu-W joint, brazed at 1125°C (2057°F) for 8 min, in Fig. 4.

Fig. 7 — Oblique section of plate-like phase in Fe-BCu-W joint at 100 µm (0.004 in.), brazed at 1125°C (2057°F) for 32 min. X100 (reduced 42% on reproduction)

Fig. 8 — (right) X-ray diffraction patterns of Mo and W tips, sheared.
in Fe-Mo phase diagram, γ-Fe, α-Fe, Fe₇Mo₆ and W in Fe-W phase diagram.

Figures 9 and 10 show detailed EPMA line analyses of both plate-like and white phases at the Mo and W base metal boundaries, respectively. From Fig. 9, it became evident that the plate-like phase deposited on Mo base metal consists of 10 to 16% Mo, 3 to 4% Cu and the rest Fe in which, however, the high Cu part exists as a spot, and the white phase formed in Mo base metal consists of 46 to 43% Fe, 1 to 0.4% Cu and the rest Mo. Therefore, according to the data in Figs. 2, 8 and 9, it can be concluded that, in a Fe-BCu-Mo joint, the plate-like phase is a Fe-Mo solid solution, α-Fe, containing a small amount of Cu, and the white phase is an intermetallic compound, Fe₇Mo₆, containing a little Cu.

When the plate-like phase reaches the insular phase in nearby Fe base metal as seen in Figs. 3 and 9, the skin-like black phase appears at the plate-like phase/filler metal interface. Since this skin-like phase consists of 11 to 9% Cu, 2 to 3% Mo and the rest Fe, it would be γ-Fe (α-Fe at room temperature) same as the insular phase which has similar composition. It should be noted that the intermetallic compound, Fe₇Mo₆, was also formed in and around the grain boundary of the plate-like phase as can be recognized in Fig. 9. This might be caused by increasing Mo concentration over the solubility limit of α-Fe at the brazing temperature; this is because the diffusion of Mo at the grain boundary from Mo base metal is considerably faster than that within the grain.

From Fig. 10, it is evident that the plate-like phase deposited on W base metal is made of two layers: the outer layer adjacent to Cu filler metal consisting of 10 to 9% Cu, 1 to 2% W and the rest Fe, and the inner one consisting of 9 to 8% Cu, 3 to 9% W and the rest Fe. Also, the white phase formed in W base metal consists of 30 to 28% Fe, 2 to 1% Cu and the rest W. Based on the experimental results in Figs. 2, 8 and 10, it can be concluded that the outer and inner layers of the plate-like phase are a Fe-W-Cu solid solution, γ-Fe (α-Fe at room temperature) and α-Fe, respectively; the white phase is an intermetallic compound, Fe₇W₆, containing a little Cu.

Figures 11 and 12 show the effect of joint clearance on the growth of both plate-like and white phases in Fe-BCu-Mo and -W joints. Comparison of Figs. 11 and 12 with the specimens brazed for 32 min in Figs. 3 and 4, respectively, reveals that the joint clearance in the range of 50 to 150 μm (0.002 to 0.006 in.) does not affect significantly the growth of both phases in either case; this differs widely from dissimilar C steel brazing (Ref. 3), where the joint clearance exerts the great influence on the growth of the columnar deposited phase. Cracks at the white phase-W base metal interfaces in Figs. 10 and 12 may result from thermal expan-
As already elaborated in the literature (Ref. 3, 7, 8), the dissolution and deposit of base metal is caused by the difference between the bonding force of both base metals (Fe-Mo or Fe-W) and that of base metal-filler metal (Fe-Cu) in molten filler metal (Cu). In order to continue this phenomenon, however, the base metal component (Mo or W) must appear at the surface of the deposited phase by diffusion, otherwise the molten filler metal is isolated from the base metal (Mo or W) boundary by the deposited phase. Moreover, the solute metal (Fe) dissolved into molten filler metal must travel to the filler metal-deposited phase interface. Hence, the velocity of the dissolution and deposit depends on the diffusion rate of either the base metal component (Mo or W) in the deposited phase under narrow joint clearance or the solute metal (Fe) in molten filler metal under wide joint clearance.

Figures 13 and 14 show plots of the thickness of both plate-like and white phases at the same time are 42 × 10⁻⁴ cm (0.00168 in.) and 5 × 10⁻⁴ cm (0.0002 in.) from equation (1); these values are nearly equivalent to those calculated above, respectively.

It may be concluded that the growth of both plate-like and white phases in Fe-BCu-Mo joint depends on the diffusion of Mo in aFe and Fe in Fe₇Mo₆, respectively. Therefore, the little influence of joint clearance on the growth of the plate-like phase, as stated earlier, is due to the fact that the diffusion rate of Fe in liquid Cu, \( D_{Fe-Cu} = 4.2 \times 10^{-5} \) cm²/s (Ref. 10), is greater than \( D_{Mo-Cu} \) and \( D_{Fe-Mo} \). The diffusion rate of C in γFe, \( D_{C-γFe} = 1.5 \times 10^{-6} \) cm²/s (Ref. 11), is nearly equal to \( D_{Fe-Mo} \) so that the growth of the columnar deposited phase in the dissimilar C steel joint was affected seriously by the joint clearance. In the meanwhile, the white phase, Fe₇Mo₆, was formed by the penetration of Fe from the plate-like phase to the Mo base metal.

As with the Fe-BCu-Mo joint, the white phase (Fe₇W₆), in the Fe-BCu-W joint was formed by the penetration of Fe from the plate-like phase to the W base metal. This is because its K value in Fig. 14 is almost identical with that for Fe-Mo₆.

Comparing the Fe-BCu-Mo and W joints, the large difference of the growth of plate-like phase might be caused by the faster diffusion rate of Mo in the plate-like phase vs. that of W. Also, the small difference of the growth of white phase was probably due to the similar diffusion rate of Fe in both white phases.

Even though the plate-like phase of Fe-BCu-Mo joint consists of only one phase i.e., aFe, the initial phase deposited on Mo base metal is believed to be γFe from the mechanism of the dissolution and deposit. However, as Mo concentration of the plate-like phase rapidly increases by the faster diffusion of Mo from the Mo base metal, this phase must be converted to aFe whose solubility limit of Mo is greater than that of γFe.
Fig. 13—Relation between thickness of plate-like or white phase and heating time in Fe-BCu-Mo joints at 50 μm (0.002 in.), brazed at 1125°C (2057°F).

Fig. 14—Relation between thickness of plate-like or white phase and heating time in Fe-BCu-W joints at 50 μm (0.002 in.), brazed at 1125°C (2057°F).

Fig. 15—Effect of thickness of Ni plating on 0.11% C st.-BCu-Mo joints at 50 μm (0.002 in.), brazed at 1125°C (2057°F) for 4 min. X200 (reduced 43% on reproduction)
Fig. 16 - Effect of thickness of Ni plating on 0.11% C st.-BCu-W joints at 50 μm (0.002 in.), brazed at 1125°C (2057°F) for 4 min. X200 (reduced 43% on reproduction)

Fig. 17 - Microstructures and EPMA line analyses of Ni-BAg-Mo (1000°C (1832°F) X 2 min) and Ni-BCu-Mo (1125°C (2057°F) X 4 min) joints at 50 μm (0.002 in.). X200 (reduced 42% in reproduction)

Fig. 18 - Microstructures and EPMA line analyses of Ni-BAg-W (1000°C (1832°F) X 2 min) and Ni-BCu-W (1125°C (2057°F) X 4 min) joints at 50 μm (0.002 in.). X200 (reduced 41% on reproduction)
γ → α conversion is accompanied with the discharge of excess Cu in γFe because of the smaller solubility limit of Cu in αFe; it may result in the formation of the high Cu part, as shown in Fig. 9.

Although these results were conducted with Cu filler metal, it has been experimentally confirmed that the similar results are obtained by silver brazing with BAg-8 filler metal.

Effect of Ni Plating

Figures 15 and 16 show the effect of Ni plating on the microstructures of 0.11% C st.-BCu-Mo and -W joints and EPMA line analyses indicated by the arrows, respectively.

In the case of the 0.11% C st.-BCu-Mo or -W joint without Ni plating, the configuration of the dissolution and deposit is quite similar to that in Fe-BCu-Mo or -W joint in Fig. 3 or 4; the 0.11% C steel base metal dissolves into molten Cu filler metal and, simultaneously, the Fe-Mo-Cu alloy consists of αFe or Fe-W-Cu alloy consists of γFe and αFe or γFe-W base metal are not formed. Obviously, the character of the microstructure in Fig. 17 and 18 varies with the filler metal used in both cases.

According to Cu-Ni and Ag-Ni phase diagrams in Fig. 19 (Ref. 5), Ni dissolves into liquid Cu or Ag up to 6 or 0.2% (Ref. 12) and also forms a solid solution containing a maximum of 91% Cu or 3% Ag at each brazing temperature, i.e., 1125 or 1000°C (2057 or 1832°F). At the same time, according to Ni-Mo and Ni-W phase diagrams in Fig. 19, Ni also forms a solid solution containing a maximum of 36% Mo or 38% W at 1125°C (2057°F) and 33% Mo or 38% W at 1000°C (1832°F), respectively.

When the molten filler metal, Cu or Ag, flows into the narrow joint clearance between Ni and Mo or W base metal, Ni dissolved in the molten filler metal from the Ni base metal diffuses to the Mo or W base metal boundary and then touches it. On touching, Ni in molten Cu could not combine with Mo or W at the base metal-filler metal interface, but Ni in molten Ag could combine with that to form the Ni-Mo or Ni-W alloy—i.e., the bonding force of Ni-Mo or Ni-W would be significantly larger than that of Ni-Ag in liquid Cu, but smaller than that of Ni-Cu, which forms a homogeneous solid solution in liquid Cu.

Because the supply of Ni to the Mo or W base metal boundary has continued through liquid Ag, the concentration of Ni-Mo or Ni-W alloy in liquid Ag gradually increases and finally exceeds its equilibrium quantity; this can be regarded as occurrence of a constitutional supercooling. Consequently, excess Ni-Mo or Ni-W alloy deposits at that boundary without temperature gradient.

According to Fe-Cu phase diagram in Fig. 2, Fe dissolves into liquid Cu up to 3%; simultaneously, liquid Cu penetrates into Fe up to 9% forming a solid solution, γFe. Also, according to Fe-Mo and Fe-W phase diagrams in Fig. 2, Fe forms solid solutions, γFe and αFe containing Mo or W up to 1% Mo or 4% W and 17% Mo or 10% W, respectively.

Concerning the phase diagrams in Figs. 2 and 19, it can be considered that, in Fe-BCu-Mo and -W joints, the relations between both base metals, and between base metal and filler metal, are similar to those in Ni-BAg-Mo and -W joints, discussed earlier. In both Cu and Ag brazing, the dissolution and deposit takes place; the Fe or Ni alloy phase deposits on the Mo and W base metals.

It is seemed certain that Fe dissolved into liquid Cu exists as a cluster (Ref. 13) (hereinafter called "associated compound"—Ref. 14). When plating Fe with Ni, Ni in addition to Fe dissolves into liquid Cu so that Fe-Ni associated compound would be formed. Since the Fe-Ni associated compound contains Ni whose bonding force to Cu must be large because of the formation of homogeneous solid solution as shown in Fig. 19, its bonding force to Mo or W in liquid Cu would be smaller than that of Fe associated compound; this decrease in the bonding force may cause the restraint of the dissolution and deposit.

*Weight-% of Ni in Cu supposing that 1.1 μm (0.000044 in.) thick Ni layer completely dissolved into molten Cu at 50 μm (0.002 in.) joint clearance.
As the Ni content of Fe-Ni associated compound increases with increasing the thickness of Ni plating, the bonding force of (Fe-Ni)-Mo or -W becomes smaller so that the further decrease in the growth of deposited phase occurs. Finally, since its bonding force probably becomes less than that of (Fe-Ni)-Cu in the case of 4.3 μm (0.000172 in.) thick Ni plating, Fe-Ni associated compound is not able to combine with Mo or W — that is, the dissolution and deposit does not take place any longer.

Shear Strength

Figure 20 shows the effect of heating time and 2.2 μm (0.000088 in.) thick Ni plating on shear strength of 0.11% C st.-BCu-Mo and -W joints. Also, Figures 21 and 22 show the typical cross-sectional microstructures of these specimens after shear test.

From Fig. 20, the shear strengths of 0.11% C st.-BCu-Mo and -W joints were about 301 MPa (43.7 ksi) and about 307 MPa (44.5 ksi), regardless of heating time. Due to Ni plating, however, the shear strengths of the joints increased to 393 MPa (57.0 ksi) and 349 MPa (50.6 ksi) respectively.

The destruction of 0.11% C st.-BCu-Mo joint occurred at the white phase/base metal interface or the Cu layer/plate-like phase interface, as shown in Fig. 21. On the other hand, in the case of 0.11% C st.-BCu-W joint the destruction of the joint occurred at the white phase/base metal interface or in the W base metal, as shown in Fig. 22.

Figure 23 shows the effect of the thickness of Ni plating on the shear strength of 0.11% C st.-BCu-Mo and -W joints. Also, Figure 24 shows the shear-ruptured microstructures of 4.3 μm (0.000172 in.) thick Ni plated specimens.

As the thickness of Ni plating increased, the shear strength of 0.11% C st.-BCu-Mo and -W joints increased from 295 MPa (42.8 ksi) to 432 MPa (62.6 ksi) and from 309 MPa (44.8 ksi) to 352 MPa (51.1 ksi), respectively. The destruction of Ni-plated specimens occurred either at the white phase-Mo and -W interfaces or in the white phase when Ni plating was less than 2.2 μm (0.000088 in.), and at the Cu layer-Mo and -W base metal interfaces in the case of 4.3 μm (0.000172 in.) thick Ni plating, as shown in Fig. 24.

Since the effect of Ni plating on the shear strength of 0.11% C st.-BCu-Mo joint was greater than that in the case of 0.11% C st.-BCu-W joint, strengthening the Mo base metal-filler metal boundary with Ni plating might be considerably large when compared to the W base metal-filler metal joint.

It can be concluded that the increase in the shear strength of 0.11% C st.-BCu-Mo and -W joints by plating 0.11% C steel base metal with Ni is due to:

1. Deterring the occurrence of the dissolution and deposit which results in the formation of both plate-like and white phases.
2. Improving the mechanical properties of the phases by alloying Ni even though the dissolution and deposit takes place in case of thin Ni plating.
3. Strengthening the Cu layer by alloying with Ni.

Conclusion

1. In the Cu brazing of Fe to Mo or W, a "dissolution and deposit of base metal" takes place. The Fe base metal dissolves into molten Cu filler metal and, simultaneously, the dissolved Fe deposits as plate-like Fe-Mo-Cu or Fe-W-Cu alloy phase from the Mo or W base metal under a constant brazing temperature.
2. Since Fe of the deposited phase penetrates into the Mo or W base metal, an intermetallic compound phase, FeMox or FeWx, is formed at that base metal boundary.
3. The Ni plating of 1.1-4.3 μm (0.000044-0.000172 in.) thickness on Fe base metal to be joined restrains the...
dissolution and deposit of base metal. Moreover, it improves the mechanical properties of both deposited and intermetallic compound phases by the alloying with Ni. Then, the shear strength of the brazed joint increases markedly.

References

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Weldability and Fracture Toughness of Quenched and Tempered 9% Nickel Steel: Part I—Weld Simulation Testing
by A. Dhooge, W. Provost and A. Vinckier

An investigation on the weldability of a quenched and tempered 9% Ni steel using weld simulation and artificial aging to estimate the heat-affected zone ductility at cryogenic temperatures is reported in Part I. Charpy-V bars were subjected to various weld simulation cycles and subsequent heat treatments and, after notching, broken at a range of cryogenic temperatures.

Weldability and Fracture Toughness of Quenched and Tempered 9% Nickel Steel: Part II—Wide Plate Testing
by A. Dhooge, W. Provost and A. Vinckier

In addition to standard impact and tensile tests, a large number of wide plate specimens welded with various consumables and welding processes were tested to evaluate the toughness and defect acceptability of 9% Ni steel in plate thicknesses greater than 25 mm.

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