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Nickel Base Filler Metals of Low Precious Metal Content

Investigation yields two filler metals that contain only about half the gold or palladium found in corresponding filler metals that have been in use

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Introduction

Applications of high temperature brazing require a basic knowledge of the properties and brazeability of available filler metals. Such applications are to be found in highly specialized and in conventional industries; nickel base filler metals as well as precious metal base filler metals are used in both instances.

Price increases for precious metals and the demand for improved ductility of nickel-base filler metals have led to the development of new nickel-base filler metals containing certain amounts of precious metals like gold or palladium. These filler metals are a combination of the nickel-chromium-boron-silicon and the high gold- or palladium-containing nickel-base filler metals.

This paper reports on investigations concerned with optimizing the composition of these new types of filler metals. It was desirable to minimize the precious metal content and to lower either the brazing temperature and the hard phases in brazed joints.

An investigation was carried out on the phase formation and melting behavior dependence on the alloy compositions for two systems:

1. Nickel-gold-chromium-boron-silicon-iron.
2. Nickel-palladium-chromium-boron-silicon-(iron).

Brazing and tensile tests (AWS standard method) were conducted with optimized filler metals, and results were compared with the known filler metals Pd-36 (Refs. 1, 2) and Au-6 (Ref. 3)—Tables 1 and 2.

Experimental Work

Ni-Pd-Cr-B-Si-(Fe) System Filler Metals

Samples were prepared by resistance heat melting under an argon atmosphere. The melting behavior of the alloys was determined by differential thermal analysis under argon atmosphere with a heating and cooling rate of 5°C (9°F) per minute (min). Micrograph analysis and

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Table 1—Low-Content Palladium Filler Metal Nominal Compositions and Melting Ranges

	Pd-36	Pd-36M	NiPd-1	NiPd-2
Composition, wt-%:				
Pd	36.8	36	34.7	19.6
Cr	11	10	10.4	8.8
Si	2.2	1	7.8	6.9
B	2.4	3	2.2	2.5
Ni	Bal.	Bal.	Bal.	Bal.
Melting range:				
°C	818 to 992	825 to 955	832 to 914	838 to 966
°F	1504 to 1818	1517 to 1751	1530 to 1677	1540 to 1771

Table 2—Low-Content Gold Filler Metal Nominal Compositions and Melting Ranges

	Au-6	NiAu-1	NiAu-2
Composition, wt-%:			
Au	20.5	19.9	10.7
Cr	5.3	5.7	5.8
Si	3.4	4	5.3
Fe	2.3	3.6	3.2
B	2.3	2.5	2.8
Ni	Bal.	Bal.	Bal.
Melting range:			
°C	943 to 960	947 to 959	943 to 950
°F	1729 to 1760	1737 to 1758	1729 to 1742

electron microscope investigations were used to determine the phase formation of the alloys.

When modifying multicomponent filler metals, it is necessary to consider the phase formation of basic ternary and quaternary systems such as nickel-boron-silicon (Ref. 4), nickel-chromium-silicon (Ref. 5), nickel-chromium-boron (Ref. 6), and nickel-chromium-boron-silicon (Ref. 7). Starting with this knowledge, it is possible to choose the alloy contents with respect to optimized melting behavior. It is also possible to estimate the solubility limits of boron and silicon in the nickel-palladium-chromium-(iron) matrix to avoid the stabilization of brittle hard phases like borides and silicides.

Boron and silicon form low melting eutectics with palladium. This gives liquidus temperatures lower than 1000°C (1832°F) for Ni-Pd-Cr-B-Si-(Fe) filler metals. The results are lower thermal influences on the base metals that are used and energy savings with the brazing process. A certain amount of chromium in these filler metals is necessary for mechanical strength and the corrosion and oxidation resistance of brazed joints.

Investigative work started with nickel alloys where the palladium concentrations were held at 36, 20 and 10 wt-%, respectively. The nickel, chromium, iron, boron and silicon were systematically varied to yield a filler metal with optimized precious metal content. Melting analysis shows a number of filler metals with good melting behavior. Compared to conventional nickel-base filler metals, the optimization of precious metal content provided alloys with increased ductility and improved filling ability of wider joint clearances without stabilization of hard phases (Ref. 8).

Two of the modified filler metals — identified as NiPd-1 and NiPd-2 — are introduced in this paper. Table 1 compares them to known filler metals Pd-36 and Pd-36M with respect to composition and melting behavior.

Brazing Tests. Tests were conducted with modified nickel-base filler metals NiPd-1 and NiPd-2 (Table 1) to determine the formation of hard phases in the braze.* Another objective was to study

*"Braze" is used here to mean "the width of the filler metal solid solution zone after brazing." The term "brazing seam," as used in the illustrations, has the same meaning.
**1 mbar = 0.6 torr = 600 microns = 0.0019 psi.

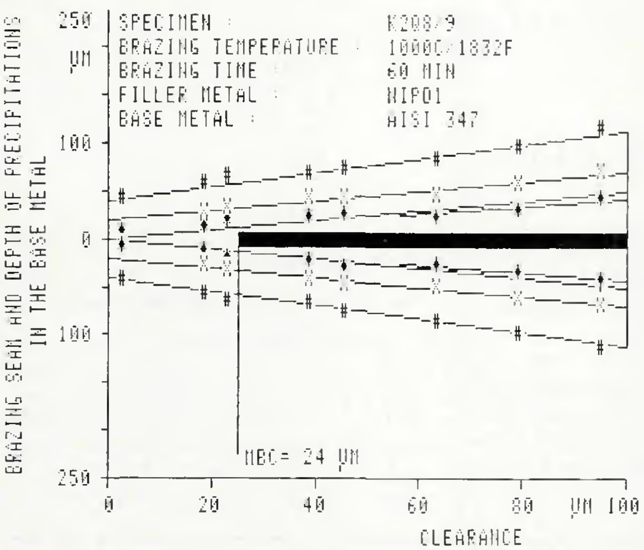

Fig. 1 — Wedge gap diagram for NiPd-1 filler metal/Type 347 stainless steel base metal after brazing in vacuum ($<10^{-4}$mbar) for 60 min

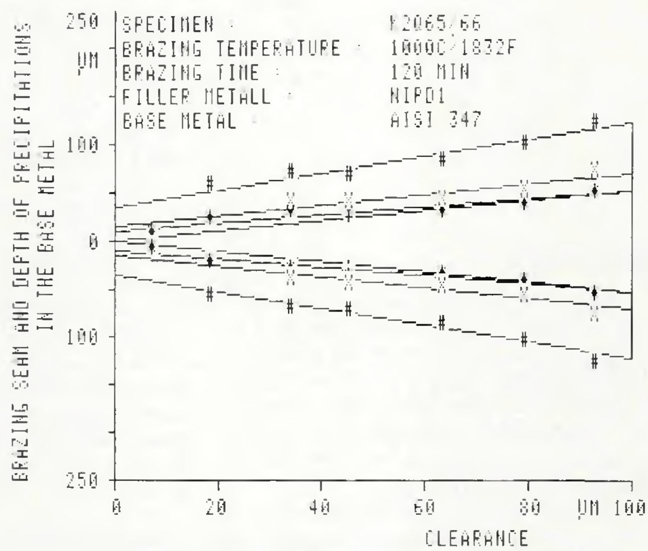

Fig. 2 — Wedge gap diagram for NiPd-1 filler metal/Type 347 stainless steel base metal after brazing in vacuum ($<10^{-4}$ mbar) for 120 min

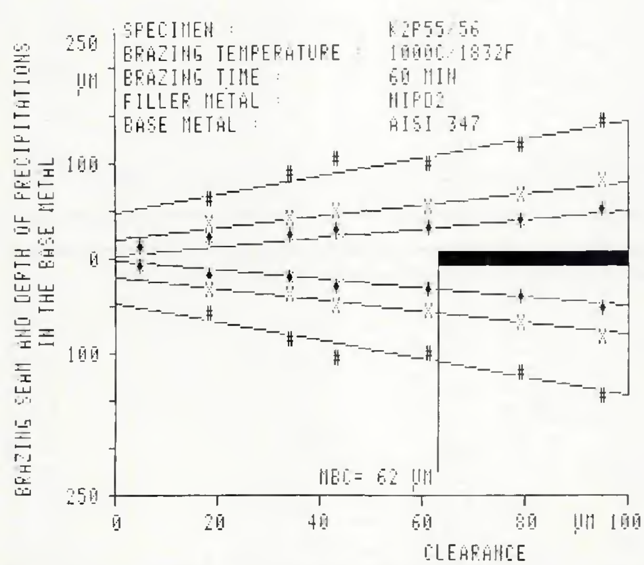

Fig. 3 — Wedge gap diagram for NiPd-2 filler metal/Type 347 stainless steel base metal after brazing in vacuum ($<10^{-4}$ mbar) for 60 min

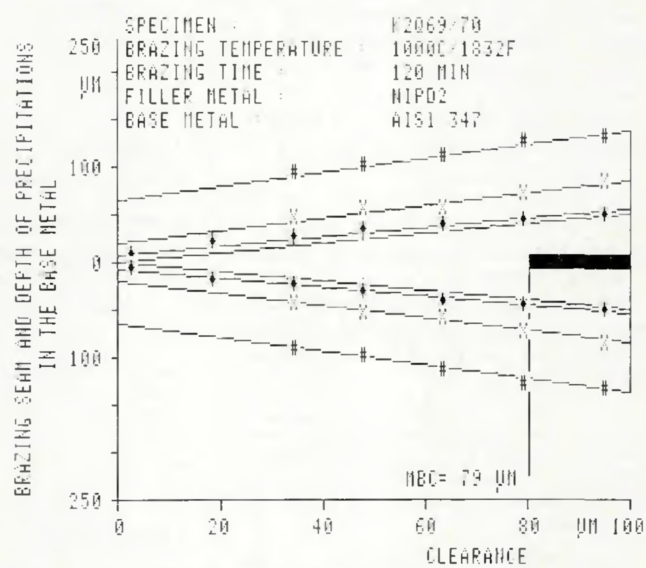

Fig. 4 — Wedge gap diagram of NiPd-2 filler metal/Type 347 stainless steel base metal after brazing in vacuum ($<10^{-4}$ mbar) for 120 min

the diffusion behavior between filler metal and base metal relative to brazing temperature, brazing time, and joint clearance.

All joints were brazed at 1000°C (1832°F) in a resistance heated furnace under a vacuum atmosphere better than 10^{-4} mbar.** The base metal was Type 347 stainless steel. The brazing times were 60 and 120 min, respectively. Powdered filler metal without cement was used, and the joint clearance was adjusted with spacers of Type 304 stainless steel.

Brazed wedge gap specimens were prepared for the metallographic investigations of the braze, the braze interface, and the heat-affected zone of the base metal relative to joint clearance (Ref. 9). Two spacers—one 50 μm (0.002 in.) thick, the other 100 μm (0.004 in.) thick—give a wedge shaped gap with a clearance that increased linearly from zero to 100 μm (0.004 in.). Because the spacers could be identified after brazing in the brazing seam, it was possible to calculate joint clearance at any cross section of the specimen by geometrical methods.

Interpretation of the wedge gap specimens involved the determination of braze quality, inter- and transcrystalline precipitations into base metal, as well as hard phase formation in the braze. Interpretation was accomplished by using a computer controlled micrograph analysis system (Ref. 10). The determined data were edited and printed as wedge gap diagrams.

The wedge gap diagrams show joint clearance, the braze (brazing seam in the diagrams), the formation of hard phases, and the penetration depths of precipitations in the base metal. Symbols that are similar to those shown below are used in the diagrams (see Figs. 1-4):

Joint clearance	- - - - -
Braze (brazing seam in Figs. 1–4)	- - + - -
Hard phases	▬
Trans- and intercrystalline precipitations	- - x - -
Intercrystalline precipitations	- - # - -

The brazing clearance at which damaging hard phases are observed in the filler metal is called "maximum brazing clearance" (MBC). This clearance marks the change from a ductile to a brittle braze. The beginning of broken line formation of hard phases is associated with a decrease in tensile strength of the brazed joint; this is the criterion for damage to the braze. The braze at small joint clearances is free of hard phases. With increasing clearances, single hard phases can be recognized; however, these do not lower the strength of brazed joints noticeably. Finally, hard phases with broken lines or lined formations essentially decrease the strength properties of brazed joints.

Figures 1–4 show wedge gap diagrams of Type 347 stainless steel after being brazed with NiPd-1 and NiPd-2 filler metals. The relationships between hard phase formation and brazing time are clearly shown. With joints brazed using filler metal NiPd-1 for 60 min, a maximum joint clearance of 24 μm (0.001 in.) can be obtained. Brazing for 120 min led to a "MBC" of more than 100 μm (0.004 in.). In the brazing system consisting of Type 347 stainless steel brazed with NiPd-2 filler metal, the "MBC" increase from 54 or 62 μm (0.0021 or 0.0024 in.) up to about 80 μm (0.0031 in.), is not so evident. The increase of "MBC" with increasing brazing time is caused by time-dependent solid diffusion, which eliminates hard phases in the center of the braze seam. Silicides are dissolved in the base metal; the amount of borides is reduced by distribution in the base metal.

Filler metal NiPd-2 with an obviously lowered precious metal content com-

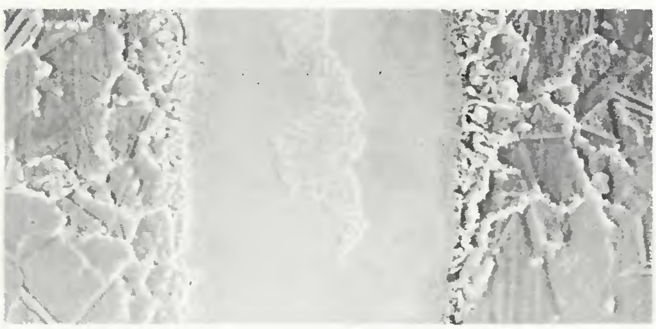

Fig. 5—SEM photomicrograph of joint brazed for 60 min at 1000°C (1832°F). Filler metal—NiPd-1; base metal—Type 347 stainless steel. Joint clearance—50 μm (0.002 in.); X600 (reduced 50% on reproduction)

Fig. 6—SEM photomicrograph of joint brazed for 120 min at 1000°C (1832°F). Filler metal—NiPd-1; base metal—Type 347 stainless steel. Joint clearance—100 μm (0.004 in.); X600 (reduced 50% on reproduction)

Fig. 7—SEM photomicrograph of joint brazed for 60 min at 1000°C (1832°F). Filler metal—NiPd-2; base metal—Type 347 stainless steel. Joint clearance—50 μm (0.002 in.); X600 (reduced 50% on reproduction)

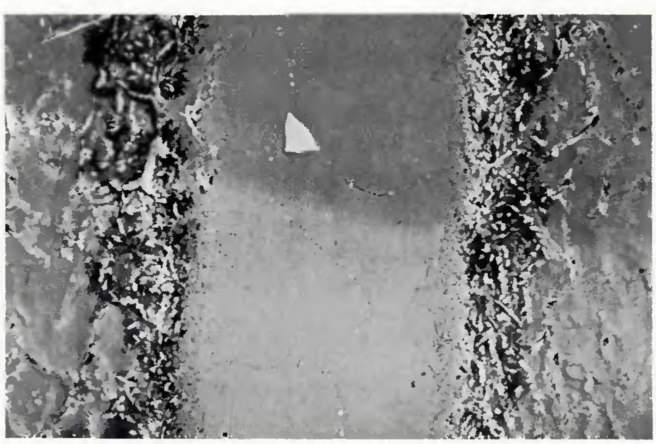

Fig. 8—SEM photomicrograph of joint brazed for 60 min at 1000°C (1832°F). Filler metal—NiAu-2; base metal—Type 347 stainless steel. Joint clearance—50 μm (0.002 in.); X600 (reduced 50% on reproduction)

pared to conventional filler metals Pd-36 and Pd-36M shows similar "maximum brazing clearances." When brazing with filler metal NiPd-1 for 120 min, it is possible to braze up to joint thicknesses 100 μm (0.004 in.) without damage by hard phases.

The wedge gap diagrams indicate how brazes are increased by diffusion and the inter- and transcrystalline boride precipitations in the base metal; this is to be considered if the joints are stressed by an alternative load.

Figures 5-7 show scanning electron micrographs of the brazed joints. The austenitic base metal shows typical twin crystals. Moreover, the grain size caused by the brazing heat treatment at 1000°C (1832°F) for 60 min has doubled compared to the nonheat treated material. An increase of the brazing time from 60 to 120 min does not show any effect on grain growth. Also, grain growth does not lead to a decrease of the tensile strength of the base metal.

Chromium boride inter- and transcrystalline precipitations in the base metal are characteristic for boron-containing filler metals. These are caused by the small solubility of the filler metal matrix for boron. These forms of precipitations could affect the dynamic characteristic values of the brazing joints as mentioned before. Furthermore, the formation of chromium borides could also reduce the chromium content of the base metal and, thereby, influence joint corrosion resistance.

The braze consists of nickel [palladium, chromium, silicon] solid solutions. Palladium solid solution could not be recognized, because nickel and palladium also form a complete solid solution at low temperatures. The microhardness of nickel solid solution in the filler metal amounts to 230-250 HV 0.05. The joint in Fig. 5 consists of Type 347 stainless steel brazed with filler metal NiPd-1 at 1000°C (1832°F) for 60 min. It shows broken line hard phases at a clearance of 50 μm (0.002 in.) as illustrated by the wedge gap diagram in Fig. 1. The hard phases consist of nickel borides with a microhardness of 1000-1200 HV 0.05 and palladium silicides with a microhardness of 900-1000 HV 0.05. The strength of brazed joints like these is lowered by the stabilization of the hard phases.

The amount of hard phases in the braze can be reduced by increasing brazing time from 60 up to 120 min — Fig. 6. At a clearance of 100 μm (0.004 in.), just a few single palladium silicides can be recognized in the center of the braze. These single hard phases do not cause any noticeable reduction of brazed joint mechanical properties. Brazed joint strengths are comparable with the strengths of the base metals.

The Type 347 stainless steel joint brazed with the filler metal NiPd-2 at 1000°C (1832°F) for 60 min shows no hard phases in the braze at a clearance of 50 μm (0.002 in.) — Fig. 7.

Ni-Au-Cr-B-Si-Fe System Filler Metals

Gold is similar to palladium in that it also forms low melting eutectics with the non-metals, boron and silicon. This was shown by Fairbanks (Ref. 3) in developing the filler metal Au-6* with the following composition, wt-%: Au — 20.5, Cr — 5.3, Si — 3.4, Fe — 2.3, B — 2.3, and nickel — balance. Based on this work, nickel-base filler metals could be developed with respect to optimized melting behavior and low gold metal content through investigation of the nickel-gold-chromium-silicon-boron-iron alloy system.

Table 2 compares two modified nickel-base filler metals of low gold content and filler metal Au-6 with respect to composition and melting behavior. Filler metal NiAu-1 is only a small modified alloy of the filler metal Au-6. However, filler metal NiAu-2 shows a reduced gold content of nearly 50% in comparison to Au-6. All filler metals have a similar melting behavior. Filler metal NiAu-2 has a composition approximating the eutectic composition of the Ni-Au-Cr-B-Si-Fe system.

Brazing Tests. Tests were carried out with optimized filler metals NiAu-1 and NiAu-2 under the same conditions used for the NiPd1 and NiPd2 filler metals.

Figure 8 shows a 50 μm (0.002 in.) wide opening of a Type 347 stainless steel joint brazed with NiAu-2 at 1000°C (1832°F) for 60 min. Because of the boron content of the filler metal, there also are inter- and transcrystalline boron precipitations in the base metal. The braze contains nickel (gold-chromium-iron-silicon) solid solutions with a microhardness of 240-250 HV 0.05.

Below a temperature of 820°C (1508°F) in the binary nickel-gold system, a miscibility gap in the solid state exists. The structure of nickel-gold alloys contains both nickel-rich and gold-rich solid solutions. Because of the miscibility gap in the nickel-gold system, some single bright gold solid solutions in the brazing seam are formed. Hard phases could not be recognized in joints brazed at 1000°C (1832°F) for 60 min at a joint clearance of 50 μm (0.002 in.).

At a clearance of 100 μm (0.004 in.), the braze is damaged by line-formed hard phases. These hard phases consist of nickel borides, nickel silicides and hard phase containing eutectic parts; its microhardness amounts between 900 and 1200 HV 0.05 — Fig. 9. Again, single bright phases in the braze are identified as gold solid solutions with a microhardness of 270 to 300 HV 0.05.

The MBC's or "maximum brazing clearances" of Type 347 stainless steel joints brazed with NiAu-1 and NiAu-2 filler metals at 1000°C (1832°F) for 60 min are 75 μm (0.003 in.) to 80 μm (0.0031 in.); this value is comparable to joints brazed with filler metal Au-6 under the same conditions. Conventional nickel-base filler metals show smaller MBC's under similar brazing conditions. For

**Au-6 . . . not to be confused with BAu6 (containing approximately 70% gold) per AWS 5.8-81.*

Fig. 9 — SEM photomicrograph of joint brazed for 60 min at 1000°C (1832°F). Filler metal — NiAu-2; base metal — Type 347 stainless steel. Joint clearance — 100 μm (0.004 in.); X600 (reduced 50% on reproduction)

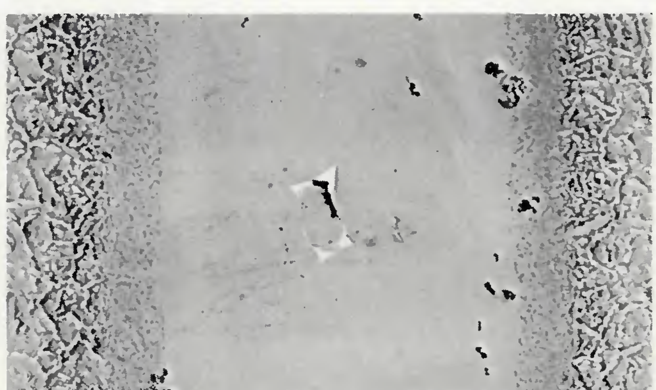

Fig. 10 — SEM photomicrograph of joint brazed for 120 min at 1000°C (1832°F). Filler metal — NiAu-2; base metal — Type 347 stainless steel. Joint clearance — 100 μm (0.004 in.); X600 (reduced 50% on reproduction)

instance, Type 316 stainless steel joints brazed with filler metal BNi-2 for 60 min at 1010°C (1850°F) show a MBC between 45 and 50 μm (0.0018 and 0.002 in.) (Ref. 9).

An increase of brazing time from 60 to 120 min exerted a beneficial effect. This was the total elimination of hard phases in Type 347 stainless steel joints brazed at 1000°C (1832°F) with NiAu-1 and NiAu-2 filler metals up to clearances of 100 μm (0.004 in.)—Fig. 10. This means that brazed joints in a clearance range of 0 to 100 μm (0.004 in.) reach tensile strengths comparable with base metal tensile strengths.

Brazed Joint Strength Tests

The mechanical strengths of high temperature brazed joints were evaluated by using metrically measured specimens comparable to those called for by the AWS standard strength test (Ref. 11). The sheet thickness was t = 3 mm (0.12 in.), and overlap-to-thickness (A/t) ratios were 0.5, 1, 2, 3, and 5.

The base metal was Type 321 austenitic stainless steel. Brazing was carried out in a vacuum better than 10^{-4} mbar at 1000°C (1832°F) for 60 min.

The results of tests carried out with the AWS standard strength test and optimized low palladium content filler metals NiPd-1 and NiPd-2 are shown in Figs. 11 and 12. Minimum overlap-to-thickness ratios equal to 3 were used with both filler metals.

The good dimensioning characteristic of filler metal NiPd-1 was surprising. As shown in Fig. 1, a "maximum brazing clearance" (MBC) of just 24 μm (0.001 in.) was obtained when Type 347 stainless steel was brazed with NiPd-1 filler metal at 1000°C (1832°F) for 60 min. Nevertheless, even at 50 μm (0.002 in.) where Fig. 1 shows damage to the braze has occurred, single-lap joint strength properties were not reduced. A comparable, higher minimum overlap-to-thickness ratio of about 5 was attained using filler metal Pd-36M.

Figures 13 and 14 provide an insight to tensile (σ) and shear (τ) stresses associated with overlapped Type 321 stainless steel joints brazed with optimized filler metals NiAu-1 and NiAu-2. As was the case with the low palladium content filler metals, overlap-to-thickness ratios of about 3 were attained.

Conclusion

The demand for ductile and low melting nickel-base filler metals, together with the precious metal market price situation, has led to the development of filler metals with low precious metal content. Thus the investigations reported in this paper concern the optimization of filler metals containing precious metals that were already in industrial use. Optimiza-

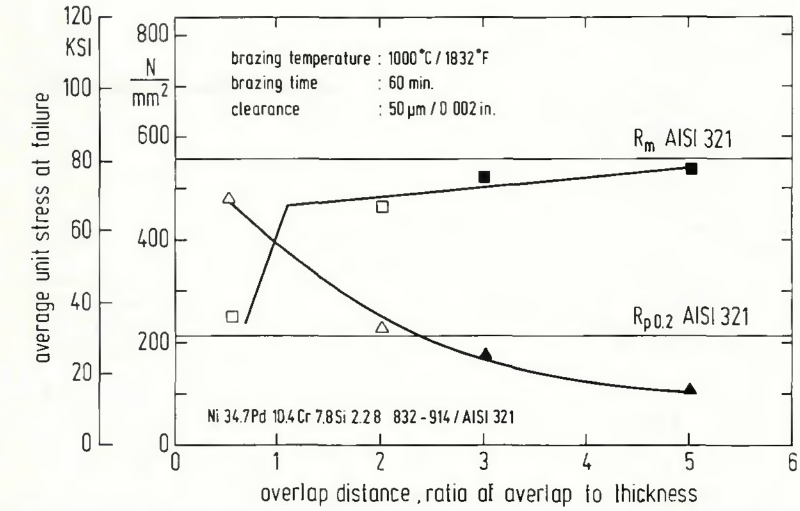

Fig. 11—Application of AWS single-lap strength test to joint consisting of Type 321 stainless steel base metal brazed with NiPd-1 filler metal. Open symbols represent failure in deposited metal; solid symbols represent failure in base metal

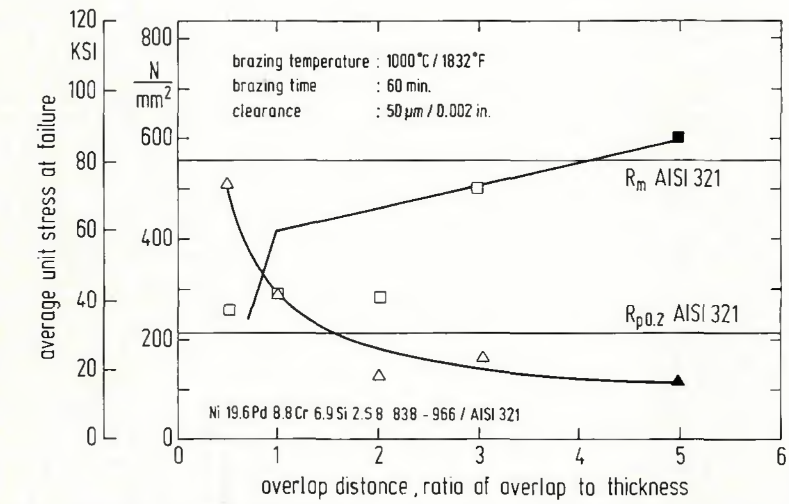

Fig. 12—Application of AWS single-lap strength test to joint consisting of Type 321 stainless steel base metal brazed with NiPd-2 filler metal. Open symbols represent failure in deposited metal; solid symbols represent failure in base metal

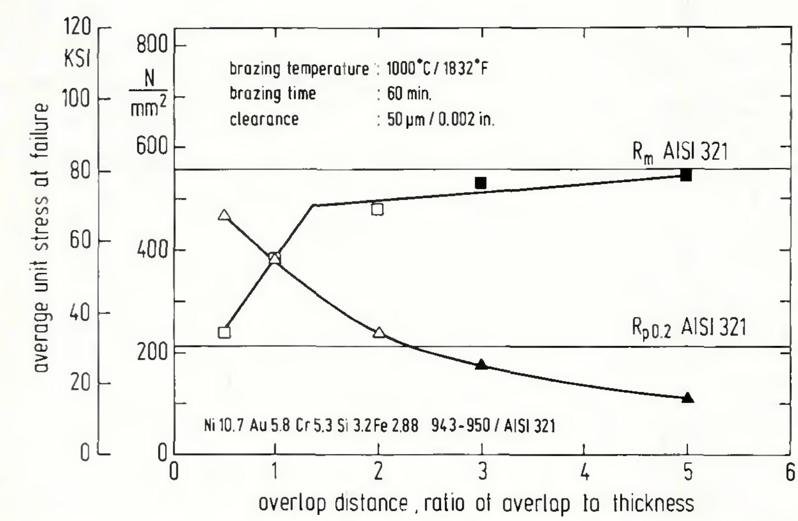

Fig. 13—Application of AWS single-lap strength test to joint consisting of Type 321 stainless steel base metal brazed with NiAu-1 filler metal. Open symbols represent failure in deposited metal; solid symbols represent failure in base metal

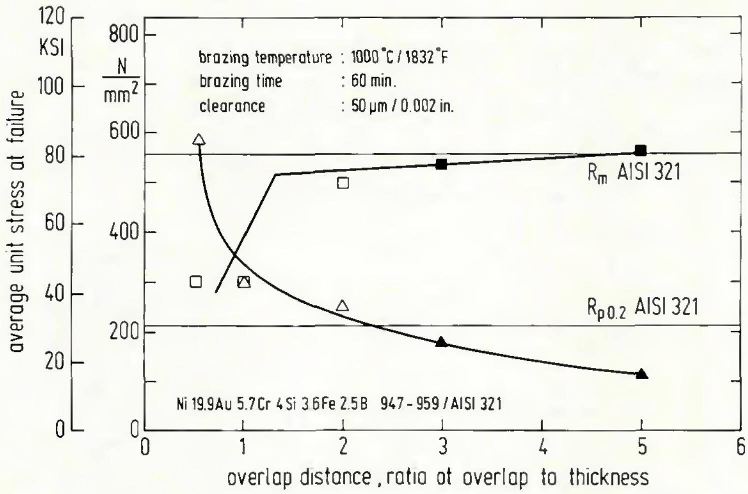

Fig. 14 — Application of AWS single-lap strength test to joint consisting of Type 321 stainless steel base metal brazed with NiAu-2 filler metal. Open symbols represent failure in deposited metal; solid symbols represent failure in base metal

tion involved the reduction of precious metal content, liquidus temperature and hard phases in the filler metals as well as obtaining constantly good brazeability. Accordingly, the structure, phase formation, and melting behavior of two alloy systems were studied; the two systems were:

1. Nickel-palladium-chromium-boron-silicon-(iron).
2. Nickel-gold-chromium-silicon-boron-iron.

Brazing tests and mechanical property determinations were conducted on joints in Types 347 and 321 stainless steel that were brazed with optimized filler metals. Results can be summarized as follows:

1. A reduction of liquidus temperatures became possible.
2. Nickel-base filler metals of low precious metal content can be brazed at an energy saving brazing temperature of 1000°C (1832°F), thereby exerting minimal thermal influence on the base metals.
3. Depending on grain size, brazing times up to 120 min do not effect an essential change in base metal mechanical properties.
4. Modification of known nickel-palladium filler metals Pd-36 and Pd36-M brings about a decrease in their melting temperatures.
5. It was possible to gradually reduce the palladium and gold content of filler metals without adverse effects relative to melting behavior or hard phases formation.
6. The compositions and melting ranges of the two filler metals that were optimized as to melting behavior and lowest precious metal content are:
   - Au — 10.7%, Cr — 5.8%, Si — 5.3%, Fe — 3.2%, B — 2.8%, Ni — balance; 943 — 950°C (1729 — 1742°F)
   - Pd — 19.6%, Cr — 8.8%, Si — 6.9%, B — 2.5%, Ni — balance; 838 — 966°C (1540 — 1771°F).
7. The low gold content filler metal alloy is nearly eutectic.

Wedge gap specimens and AWS single-lap shear specimens, using Type 347 and 321 austenitic stainless steel base metals, were brazed with optimized filler metals to determine gap-filling ability and mechanical properties. Scanning microscope analyses were conducted to characterize braze structure and to study the metallurgically influenced zones in base metals.

Acknowledgement

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