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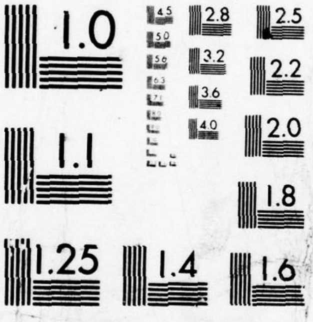

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SUBMERGED ARC WELDING OF TITANIUM

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Technical Report No. 2

1 August ~~1,~~ 1977 ~~to~~ July 31, ~~19~~78

Submitted to:

Office of Naval Research
800 N. Quincy St.
Arlington, VA.22217
Attn: Dr. Bruce MacDonald
Contract No. N00014-77-C-0569

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By:

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C.S. Chai, J.J. Gullotti ~~and~~ T.W. Eagar

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studied, indicating enhanced weld penetration in the presence of a flux. A critical review of available information on Soviet titanium fluxes is also presented.

CONTENTS

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. ABSTRACT

The submerged arc welding of titanium using CaF_2 fluxes has been studied to determine the sources of nitrogen contamination and the effect of flux purity on arc stability and weld bead shape. It is shown that plasma jet entrainment and atmospheric absorption on the hot base plate ahead of the arc prior to flux melting are the primary sources of nitrogen contamination. The arc stability is strongly dependent upon the CaF_2 purity. The high weld bead contact angle is a result of the metal transfer mode of the consumable titanium electrode. In addition, the effect of CaF_2 flux on gas tungsten arc welds has been briefly studied, indicating enhanced weld penetration in the presence of a flux. A critical review of available information on Soviet titanium fluxes is also presented.

I. INTRODUCTION

Due to its extreme chemical reactivity, fabrication of large scale titanium structures, particularly by welding, presents several difficulties. Among these is the choice of an adequate procedure for shielding the hot weld metal from almospheric gases such as oxygen and nitrogen. In the United States, the most commonly chosen process for joining titanium is gas metal arc welding, using copious amounts of very pure argon shielding gas, while in the Soviet Union, the most common technique appears to have been submerged arc welding, using special halide fluxes developed by Gurevich and co-workers.* The difference in approach by these two groups is likely due to the unavailability of large quantities of high purity argon shielding gas in the Soviet Union prior to the early 1960s.[1] Since that time Soviet researchers appear to have switched from purely submerged arc welding to what they term "semi-submerged" arc welding, using auxiliary argon shielding gas. Semi-submerged arc welding is basically a variation of the gas tungsten arc welding process, in which a small quantity of halide flux coating is used to modify the arc behavior; thereby providing more efficient use of the welding energy.

Interest in the Soviet ability to produce sound submerged arc welds in titanium has led to several studies in North America. In 1968, H.F. Petsch of the Electric Boat Division of General Dynamics Corporation carried out a study sponsored by the Naval Applied Science Laboratory. His work was an extension of a 1964 study by Canadair, Ltd of General Dynamics. Petsch found that:

1) The halide fluxes should not contain significant quantities of oxygen, nitrogen, carbon, or hydrogen [although the term significant was not quantified].

---

* A critical review of published information on Soviet titanium submerged arc welding fluxes is presented in the Appendix.

2) High purity fluoride-base fluxes with chloride additions were found to be suitable.

3) The best flux tested was composed of CaF_2-$5BaCl_2$-2LiF [although this flux was hygroscopic].

4) High oxygen content resulted in low toughness weldments.

5) The small difference in flux and metal density resulted in slag inclusions.

6) The low melting point and viscosity of the halide flux created a high flux melting rate, poor weld surface contour, lack of fusion, cold shuts, and difficulty in slag control.

7) Further developmental work was necessary.

Following Petsch's work, Union Carbide Corporation, under contract to the Office of Naval Research, made a similar study.[3] They found that:

1) Fluoride-base fluxes are required.

2) No oxide component (>2%) is tolerable.

3) Bead-on-plate screening for flux operability is not satisfactory [due to poor bead contact angle].

4) Fused CaF_2 may provide adequate shielding even without an auxiliary argon shield.

5) Fused fluxes are superior to blended fluxes.

6) Auxiliary argon shielding reduces nitrogen contamination.

7) The resulting welds have intermediate strength-toughness characteristics [compared with the best and worst base metal values].

8) Heat treating the welds at 535°C for one hour results in a small increase in toughness.

Although not stressed in the reports, each of the above investigations found the operability of the titanium fluxes to be marginal and each suggested further work in this area.

The objective of the present investigation is to determine the source and cause of oxygen and nitrogen contamination of titanium submerged arc welds and to develop methods of reducing the levels of these contaminants. As the work has progressed, efforts have been made to quantify arc stability and observations have been made concerning the operability of titanium submerged arc fluxes.

II. MATERIALS AND EQUIPMENT

All welds were made on 19mm (0.75 inch) Ti-6Al-4V ELI (extra-low interstitial) plate received from RMI Titanium Company of Niles, Ohio. The welding electrode was also Ti-6Al-4V, purchased in three diameters from Astro Metallurgical Corporation of Wooster, Ohio. The mill certifications of these materials are given in Table 1.

CaF_2 was the flux used throughout most of this investigation. Initially, reagent grade powder, of 99.95% analysis, obtained from Baker Chemical Company, was induction melted in 2020 grade graphite crucibles under argon. However, subsequent X-ray analysis indicated that this fusion technique resulted in 1 to 3% CaO impurity formation from adsorbed water vapor, by the reaction

$$CaF_2 + H_2O \rightarrow CaO + 2HF\uparrow .$$

It was later found that this quantity of CaO in the CaF_2 flux was detrimental to the arc stability of the flux.

In order to obtain oxygen free CaF_2 flux from this reagent grade powder, it was necessary to sinter the flux in a graphite lined Inconel furnace, while passing purified HF gas at 800°C. This procedure, which is used in the production of optical quality fluoride crystals, produces CaF_2 with an oxygen content below 100 ppm. Other CaF_2 purification techniques are also known, but generally are not as effective as the above technique.[4]

After discovery of the improved operating characteristics of very pure CaF_2, studies were performed with crushed and screened optical grade crystal lumps purchased from Optovac, Inc., of North Brookfield, Massachusetts.

Two separate welding power supplies were used in this study. The first was a Linde SVI-300, which provided a range of control of the circuit inductance. The second power supply, a Linde VI-800, has a fixed inductor; however, the inductor in the VI-800 is much larger than the one in the SVI-300 and hence produces a more stable arc.

The as-received plate was plasma flame cut into 0.3 x 0.3m plates for bead-on-plate weld testing. Individual weld samples were removed from these test plates by sawing and grinding, using SiC wheels.

III. POSSIBLE SOURCES OF NITROGEN CONTAMINATION

In submerged arc welding there are two sources of nitrogen contamination, viz., atmospheric nitrogen and nitrogen dissolved in the flux. In order to determine which of these sources is primary, various transport mechanisms must be hypothesized and tested. The sources which were studied in this investigation are listed below.

1. Atmospheric sources

Five separate mechanisms of atmospheric nitrogen contamination were considered. They were:

a. Diffusion of nitrogen through the flux.

   Although generally a slow transport process, diffusion in low viscosity, rapidly moving, halide slags may be sufficient to transport the relatively small quantities of nitrogen (several hundred ppm) found in titanium submerged arc welds.

b. Absorption of nitrogen ahead of the arc in hot regions not yet protected by molten flux.

   A region of the titanium plate immediately ahead of the welding arc will be heated to temperatures sufficient to absorb atmospheric gases prior to melting of the flux cover. The ambient atmosphere between the flux granules will contact this hot titanium, react on the surface, and subsequently be melted into the weld pool as the arc passes.

c. Absorption of nitrogen on the hot electrode emerging from the contact tip.

   The large welding currents and high electrical resistivity of titanium causes severe heating of the electrode, hence, the distance from the end of the electrode to the contact tip (stick out) is very important. If the stickout is large, the electrode may be heated to temperatures sufficient to cause absorption of atmospheric gases on the surface.

d. Failure of flux shielding due to slag runoff.

   The low viscosity halide slags are not as effective in maintaining cover for the molten weld pool as are the more viscous silicate slags used in welding steel.

e. Entrainment of atmospheric gases into the arc cavity due to plasma jets.

   Runoff of the molten slag near the electrode is enhanced by the increased convection caused by electromagnetic forces inherent in the arc. This convection is termed a plasma jet. The jet creates a pumping action which may pull atmospheric gases into the weld cavity.

2. Flux sources

It is possible, although not probable, that the fused CaF_2 flux may contain dissolved nitrogen. Since such nitrogen would be expected to be physically dissolved rather than chemically dissolved, this source would probably not produce a large quantity of nitrogen; however, all flux was fused under argon in order to prevent any such contamination.

IV. RESULTS OF NITROGEN CONTAMINATION STUDIES

A series of welds was made using argon induction melted reagent grade CaF_2. (This material was later found to contain 1% CaO.) After fusion, the CaF_2 was crushed and screened to the desired size, usually 80 to 120 mesh (approximately 0.15 mm diameter). In order to isolate the effects of atmospheric absorption on either the base plate or the electrode, anodizing of the titanium was performed. It was found that the anodized oxide layer remained intact up to very high temperatures as indicated by the molten electrode tip shown in Figure 1. It is seen in this Figure that the anodized layer is not removed until the final 4 to 5 mm of electrode is reached, hence, anodized electrodes provide an effective method of protecting the titanium metal surface from nitrogen absorption caused by long stickout (source c). Similarly, anodizing of the base plate provides protection from nitrogen absorption on the hot metal immediately ahead of the arc (source b). The anodized layer did not interfere with the transfer of welding current from the contact tube to the electrode.

In several welds, argon shielding around the electrode was used to determine the effects of diffusion through the slag and plasma jet entrainment (sources a and e).

The results of a series of welds made with various combinations of anodized electrode, anodized base plate, electrode stickout and argon shielding are shown in Table 2. Welds 7 and 8 illustrate the harmful effects of increased electrode extension (stickout). A 20% increase in stickout results in a 30% increase in weld metal nitrogen content, hence control of the electrode extension is critical.[1] It should be noted that the electrode extension of 16 mm, used in the majority of welds, is the minimum practical limit. Further reductions in extension resulted in overheating of the contact tip and plowing through the flux burden. Additionally, such small electrode extensions limit access to the weld joint when producing groove welds.

Comparison of Welds 5 and 11 with Welds 1, 3, and 9 indicates that anodizing the electrode has very little effect, if any, on nitrogen absorption, providing the electrode extension is reduced to 16 mm.

Except for the long stickout welds (7 and 8), comparison of the odd numbered and even numbered welds in Table 2 indicates that anodizing of the base plate results in a reduction in the weld metal nitrogen content. Hence, absorption of nitrogen on the hot metal ahead of the arc was found to be one of the sources of contamination. Anodizing the base plate prior to welding provides a method of reducing this source of contamination with little or no increase in the weld metal oxygen content. This is apparent when one considers that a 10^{-7}m (1000 Å) thickness of oxide on the surface of the plate is negligible when compared to a 10^{-2} -10^{-3}m thickness of weld metal. The anodized layer would not be expected to contribute more than 50 to 100 ppm of oxygen to the resulting weld metal. This level is insignificant when compared with the several thousand ppm of oxygen already present.

Further inspection of Table 2 indicates that the greatest reductions in nitrogen contamination are provided by external argon shielding (Welds 9-12). This result indicates that either diffusion through the flux or plasma jet entrainment is responsible for the bulk of the nitrogen contamination. Later studies (Section V) using high purity fluxes indicate that the plasma jet phenomenon is the dominant mechanism.

The flux used in producing the welds listed in Table 2, exhibited very unstable arc behavior, in many cases resulting in extinction of the arc followed by an explosive restart expelling flux from the arc cavity, thereby exposing the arc to the atmosphere. The pumping action of the plasma jets then caused entrainment of nitrogen into the arc cavity. Comparison of welds 1 through 8 with welds 9 through 12 indicates that the greatest single source of nitrogen contamination was unstable arcing leading to plasma jet entrainment. The second greatest problem was the very rough weld bead produced under these conditions. Examples of these beads are shown in Figure 2.

It should be noted that the oxygen content of the welds listed in Table 2, remains relatively constant in spite of the wide variations in nitrogen content. This is apparently caused by a slight refining action of the flux on weld metal oxygen. It was found in the present study that optical quality CaF_2 resulted in 1300-2000 ppm oxygen in the weld metal and CaF_2 - 1% CaO resulted in 2000-3000 ppm oxygen. A report in the Soviet literature claims that the addition of 40% LaF_3 to a CaF_2 based flux results in a 30% reduction in weld metal oxygen content compared to the parent metal values.[7] Hence, halide fluxes of sufficient purity and proper composition provide an effective means of controlling the weld metal oxygen content, but fail to control the weld metal nitrogen content.

V. FLUX PURITY

Following the results of the nitrogen contamination study, work concentrated upon understanding the cause of arc instability. A review of the Soviet literature,[5,6] indicated that very modest levels of CaO impurity (>0.5%) could create unstable arc behavior in titanium welding. An x-ray analysis of the flux fused in argon indicated that the flux, which was used for the nitrogen contamination studies, contained 1 to 3% CaO as an impurity. In order to test the Soviet claim, optical quality CaF_2 crystals were obtained. The results of welds made with various CaF_2 purity are shown in Table 3. The very low nitrogen contamination levels observed without argon shielding indicates that nitrogen diffusion through the slag is unimportant. Hence, the primary source of nitrogen contamination is arc instability and subsequent plasma jet entrainment of atmospheric gases.

A practice commonly used in industry is to evaluate the extent of titanium weld contamination by external weld bead color. Table 3 illustrates that such estimates of interstitial contamination are not reliable. It can be seen that weld 1A, although lusterous in appearance, has a much higher level of contamination than Weld 5A, which had a darkly oxidized surface. Hence, surface bead appearance may lead to erroneous conclusions as to the bulk contamination levels.

VI. ARC STABILITY

1. Measurement

In order to judge relative differences in arc stability, it is necessary to have at least a semi-quantitative technique of measuring stability. The method chosen in this study was suggested by G. Uttrachi of the Linde Division of Union Carbide Corporation. His technique utilizes a storage oscilloscope operated in the X-Y mode with the welding voltage trace plotted along the ordinate and the welding current trace plotted along the abscissa. This produces a dynamic response curve which approximates an oval oscillating around a point of average current and voltage. A schematic is shown in Figure 3. The stability is monitored by taking a time average (several seconds) of the voltage-current response. This produces an image on the storage oscilloscope indicating the range of voltage-current fluctuations. Some small fluctuations are to be expected in consumable electrode welding, due to variations in electrode melting rate, however, fluctuations intersecting the ordinate indicate periods in which the arc is extinguished. Similarly, extreme excursions of weld current beyond the average current indicate wide variations in electrode consumption rate, and possible short circuiting. A DC welding power supply with a high inductance should inhibit arc extinction, but may aggravate the problem of short circuiting. However, if short circuiting should occur, the large inductor would prevent a serious overcurrent.

All stability measurements on submerged arc welds in this report were made on a Linde VI-800 power supply possessing a large circuit inductance. Hence, it is believed that any arc extinction instabilities are due primarily to the weld metal and flux chemistries rather than power supply instabilities.

2. Results

Representative examples of the oscilloscope arc stability traces for welds made with optical quality CaF_2, CaF_2 - 1% CaO, CaF_2 - 1% NaF and CaF_2 - 1% CaO - 1% NaF are shown in Figure 4, a, b, c and d, respectively. It is seen that CaF_2 produces an unstable arc, with extinction or near extinction in every case. In addition, the voltage current characteristic appears to oscillate between two modes. These modes are:

1) The power supply load line--arc plasma mode--This is represented schematically in Figure 3 and is seen at the top of Figures 4, a-d. This mode is actually a composite of the power supply load line and the arc plasma characteristic. This is caused by the variation of arc length due to the melting of the consumable electrode. As the arc length varies, the plasma characteristics of the various arc lengths are superimposed around the power supply load line. The width of this region is also a function of the power supply inductance; the larger the inductance, the smaller the width of the region. Hence high inductance power supplies produce regions similar to Figure 3a, while low inductance power supplies produce regions similar to Figure 3b. The titanium submerged arc welds are so unstable that even a very high inductance power supply, such as the VI-800, cannot control the arc. There are times during the weld, that the arc is extinguished for periods of a second or more, as viewed on the oscilloscope trace. This undoubtedly contributes to the very rough weld beads observed in Figure 2.

2) A purely resistive mode - This mode which is indicated by lines shown in the bottom of Figure 4, a-d, includes spiking traces as the arc changes between the power supply load line and the resistive modes. The resistive mode probably results from collapse of the arc plasma, as sketched in Figure 5c. This is thought to occur in the following manner: During submerged arc welding, the plasma is contained within a flux covered cavity. The plasma pressure must be sufficient to support the flux or the flux will collapse (Figure 5c) causing the arc to be extinguished. At this point, the voltage-current trace switches from the power supply-arc plasma mode, to a purely resistive mode, with a slope determined by the electrical conductivity of the molten flux. The measured slope of this resistive mode is consistent with the published electrical conductivity of CaF_2[8].

The purely resistive mode is only observed during titanium submerged arc welding and has not been found during welding of steel. This is presumably due to the fact that the reactive titanium consumes the plasma ions, thereby reducing the plasma pressure and allowing collapse of the flux. If the welding system contains a source of volatile species, partial collapse of the flux will increase the local plasma temperature, releasing more volatile ions and stabilizing the plasma. This process is illustrated schematically by Figure 5a, b and d. It is interesting to note that no resistive mode and hence no loss of plasma ions, is noted during welding of the following:

a. a steel plate with a steel electrode and CaF_2 flux,

b. a titanium plate with a steel electrode and CaF_2 flux, or

c. a steel plate with a titanium electrode and CaF_2 flux.

In each of these cases the steel provides a source of plasma ions, whereas in a system composed solely of titanium and CaF_2, no source of ions is continuously present. The reactive titanium consumes those ions that are present and the arc is extinguished as illustrated in Figures 5 a, b and c.

Further arc stability studies were made with a non-consumable tungsten electrode. Figure 6a illustrates the oscilloscope trace obtained with a gas tungsten arc weld on titanium. In this case the shielding gas was argon. There is a fairly wide variation in the welding current, but the current never falls to zero i.e., the arc is never completely extinguished. Figure 6b shows a similar GTA weld, in which a thin layer of CaF_2 flux was present, in addition to the argon shielding gas. It is seen that the voltage variations are much greater with the CaF_2 present, although this may be partly an artifact of the GTA welder which has an arc voltage servo-controlled torch. The CaF_2 may have changed the true voltage fluctuation frequency such that the servo could not keep pace with the changes. In any case, two points are illustrated by these GTA welds tests, viz.

1) The non-consumable GTA welding arc is more stable than a consumable titanium electrode arc, when welding under CaF_2 flux, and

2) The presence of CaF_2 during GTA welding appears to be destabilizing. This is in contradiction to reports in the Soviet literature.[9]

To conclude, it appears that titanium submerged arc welding with pure CaF_2 may produce an inherently unstable arc. Some improvements in stability may be achieved by using a non-consumable electrode, but the weld bead surface remains rough and uneven. Further improvements in arc stability may be possible with modifications of the flux chemistry.

VII. WELD BEAD CONTACT ANGLE

A titanium submerged arc weld bead cross section is shown in Figure 7. The contact angle is very high; in some sections resulting in undercutting. Previous studies, varying welding parameters, were unable to alleviate this problem.[3] Since it is not obvious what causes this problem, two dissimilar metal welds were made in an attempt to isolate the cause. In one case a titanium plate was welded with a steel electrode, and in another case a steel plate was welded with a titanium electrode. Pure CaF_2 was used in each case.

The bead contact angle for the titanium electrode on steel was 85° while the contact angle for the steel electrode on titanium was 30°. This indicates that the consumable titanium electrode may be responsible for the poor bead contact angle. No explanation for this behavior is available.

VIII. GTA WELD PENETRATION

The most recent Soviet literature indicates that true titanium submerged arc welding is being replaced by semi-submerged arc welding. (See the Appendix.) The semi-submerged arc welding process is essentially a GTA weld with a thin layer ($\sim$0.5 mm) of flux present. One of the reasons for using the flux is a claim of increased weld penetration. Figure 8 shows two GTA weld cross sections: one made with argon shielding and the other made with argon plus CaF_2 flux. It is seen that the CaF_2 produces a narrower deeper weld. An adequate explanation of this phenomenon is lacking; however, it appears that the insulating solid flux restricts the arc plasma to a narrower central region. This in turn intensifies the arc heating and produces a deeper, narrower weld. The Soviet literature claims great advantages for this process.

IX. CONCLUSIONS

A study of submerged arc welding of titanium using CaF_2 as a flux has produced the following results:

1. The arc stability is a function of the CaF_2 purity. Impurities of greater than 0.5% CaO result in reduced arc stability, rough weld beads and increased nitrogen contamination.

2. The primary source of nitrogen contamination is plasma jet entrainment caused by arc instabilities. Absorption of atmospheric gases on the hot base plate ahead of the arc or on the hot electrode (due to long electrode extension) is also contributory. Anodizing of the base plate or electrode reduces the nitrogen absorption without significantly increasing the oxygen contamination.

3. CaF_2 based fluxes of sufficient purity provide refining action to control the weld metal oxygen content.

4. The surface color of the titanium weld bead is not an acceptable method of determining whether contamination of the weld metal has occurred.

5. An oscilloscope displaying the weld current and voltage in an X-Y mode provides a semi-quantitative method of measuring arc stability.

6. Titanium submerged arc welds made with CaF_2 flux are subject to an instability caused by collapse of the arc plasma. This is believed to be due to consumption of the plasma ions by the highly reactive titanium.

7. Titanium submerged arc welds produce a high bead contact angle. This is believed to be related to the metal transfer mechanism from the consumable titanium electrode.

8. The penetration of GTA arc welds on titanium may be increased by the presence of CaF_2.

In addition, a survey of Soviet literature on submerged arc welding of titanium (See the Appendix) suggests that the process was developed in response to a previous unavailability of high purity argon; however, the current availability of high purity argon has caused or is causing a switch away from this process.

References

1. H. W. Mishler, "A Review of Available Information on the Welding of Thick Titanium Plate in the USSR," DMIC Memorandum 188, March 6, 1964.

2. H. F. Petsch, "Research Study to Develop a Submerged Arc Automatic Welding Process for Fabricating Butt Welds in Thick Titanium Alloy Plate," Final Report, Contract N00140-68-C-0148 General Dynamics Corporation, Groton, Ct.

3. D. C. Hill and C. L. Choi, "Research on Materials for Submerged Arc Welding of Titanium," Final Report, ONR Contract N00014-74-0406, Union Carbide Corporation, Tarrytown, N.Y., June, 1975.

4. G. Mamantov, "Electrode Reactions in Molten Fluorides," in Molten Salts: Characterization and Analysis. Mamantov and Gleb, eds., Marcel Dekker, New York, 1969, p. 529.

5. L. K. Bosak and S. M. Gurevich, "A Non-Hygroscopic Flux for Welding Titanium and Its Alloys," Avt. Svarka. No. 5, 1966, p. 70-71.

6. S. M. Gurevich and L. K. Bosak, "The Effects of Calcium Fluoride in Type AN-T Fluxes on their Technical Properties," Avt. Svarka., No. 11, 1964, p. 47-50.

7. S. M. Gurevich, V. N. Zamkov, S. D. Zagrebenyuk and N. A. Kushnirenko, "The Effects of Fluxes Containing Rare Earth Elements on the Structure and Properties of Welds in VT15 Alloy." Avt. Svarka. No. 4, 1964, pp. 93-94.

8. I. N. Kolisnyk, "Measurement of the Electrical Conductivities of Fluxes Between 1300 and 2300°C," Avt. Svarka., 1964, No. 4, p. 10-14.

9. S. M. Gurevich, V. N. Zamkov, and N. A. Kushnirenko, "Improving the Penetration of Titanium Alloys When They Are Welded by Argon Tungsten Arc Process," Avt. Svarka., 1965, No. 9, pp. 1-4.

Table 1. Starting Materials, Base Metal and Electrodes

Base Metal

Ingot Analysis No. 803175

	C	Fe	Al	V	N	O	H
Certified	.02	.17	6.1	3.8	.012	.117	.010
Check 1	---	---	---	---	.0088	.100	---
Check 2	---	---	---	---	.0121	.176	---

Annealed 1/2 hour, 927°C, A.C. + 1 hour, 760°C, A.C.

Mechanical Properties

	Yield Strength MPa (ksi)	Tensile Strength MPa (ksi)	Elongation %
Longitudinal	863 (125)	934 (135)	13.5
Transverse	925 (134)	993 (144)	12.5

Welding Electrodes

Diameter, mm (in)	C	Fe	Al	V	N	O	H
3.2 (.125)	.019	.15	6.28	4.11	.006	.078	.002
Check 2	---	---	---	---	.010	.180	---
2.4 (.093)	.019	.15	6.28	4.11	.008	.078	.002
Check 2	---	---	---	---	.010	.180	---
1.6 (.062)	.019	.15	6.28	4.11	.008	.078	.009

Table 2

Titanium Submerged Arc Weld Series Used to Determine Nitrogen Contamination Source

Weld No.	Anodizing Schedule	Ar Shield	Electrode Extension (mm)	Volts V	Amps A	Weld Quality	% O	% N	Mean Hardness (Knoop) (500g)
1	None	No	16	35	200	Poor	0.32	0.053	391.4
2	Base Plate	No	16	35	200	Poor	0.29	0.044	389.3
3	None	No	16	30	325	Fair	0.28	0.047	385.2
4	Base Plate	No	16	30	325	Fair	0.26	0.040	379.0
5	Wire	No	16	29	350	Fair	0.29	0.053	374.5
6	Wire and Base Plate	No	16	29	350	Fair	0.27	0.046	373.6
7	None	No	19	29	325	Poor	0.28	0.063	465.8
8	Base Plate	No	19	29	325	Poor	0.33	0.069	388.4
9	None	Yes	16	29	350	Fair	0.27	0.020	368.2
10	Base Plate	Yes	16	29	350	Fair	0.29	0.016	348.2
11	Wire	Yes	16	28	350	Fair	0.23	0.016	380.4
12	Wire and Base Plate	Yes	16	28	350	Fair	0.29	0.014	341.9

Wire Size - 2.4 mm Base Plate % O 0.117 Wire % O 0.078
Flux Burden - 19 x 25 mm % N 0.012 % N 0.008
Travel Speed - 7.6 mm/s Hardness 307.8

Table 3

Effect of Flux Purity on Titanium Weld Metal Chemistry

Weld	Flux	Mesh Size	V	I	Arc Stability	Bead Appearance	O	N
1A	CaF_2 - 1.2% CaO fused.	80-120	30	400	Poor	Rough, Lusterous	0.46	.030
2A	Optical CaF_2	80-120	30	340	Fair	Smooth, lusterous	0.13	.015
3A	Optical CaF_2	8-12	28	450	Fair	mostly smooth, lusterous	0.14	.015
4A	Reagent CaF_2	325-dust	29	400	Very Poor	mostly smooth, blackened	0.42	.029
5A	Optical CaF_2 - 1% NaF	80-120	28	350	Fair	Very rough, dark, oxidized.	0.22	.022

Electrode diameter 2.4mm

Electrode extension 15mm

Travel speed 6.5mm/sec.

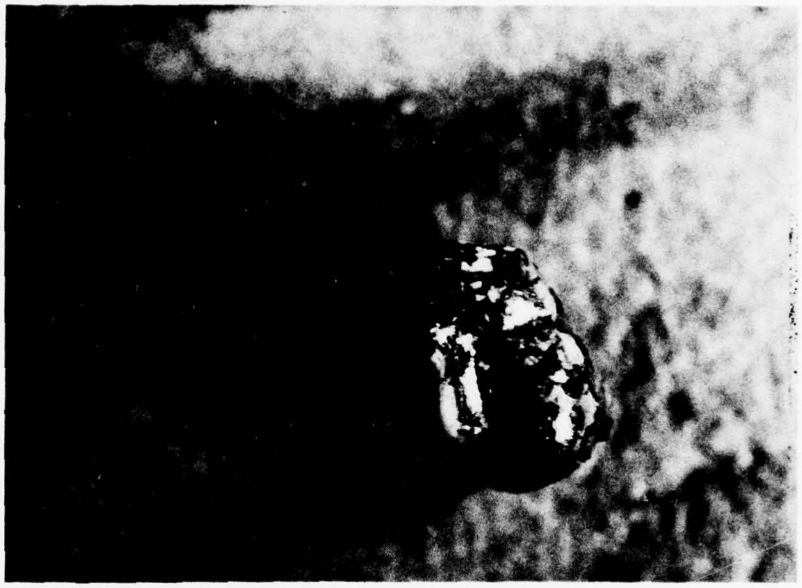


Figure 1. Tip of anodized titanium electrode used in submerged arc welding. Note that the anodized layer remains intact to within a few electrode diameters of the end of the electrode.

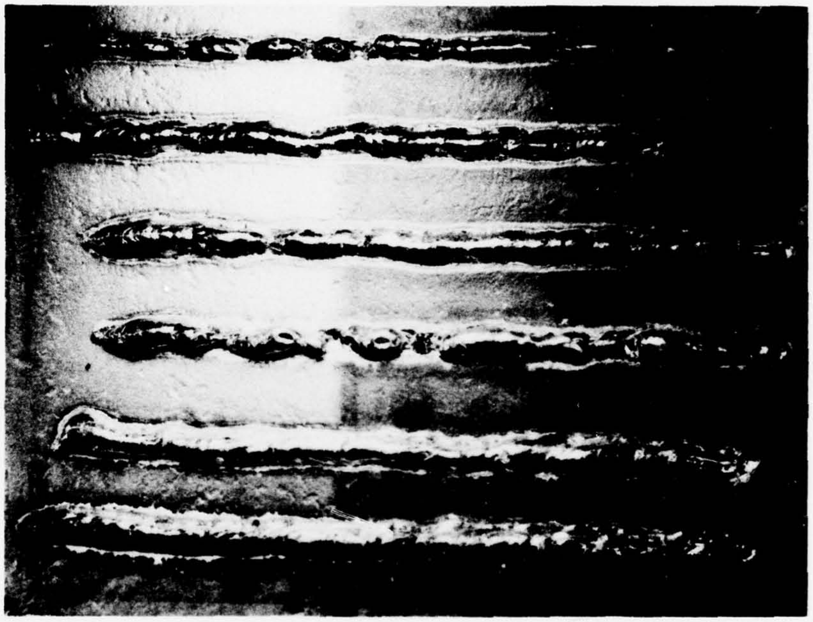


Figure 2. Titanium Submerged Arc Weld Beads Produced with CaF_2 - 1% CaO

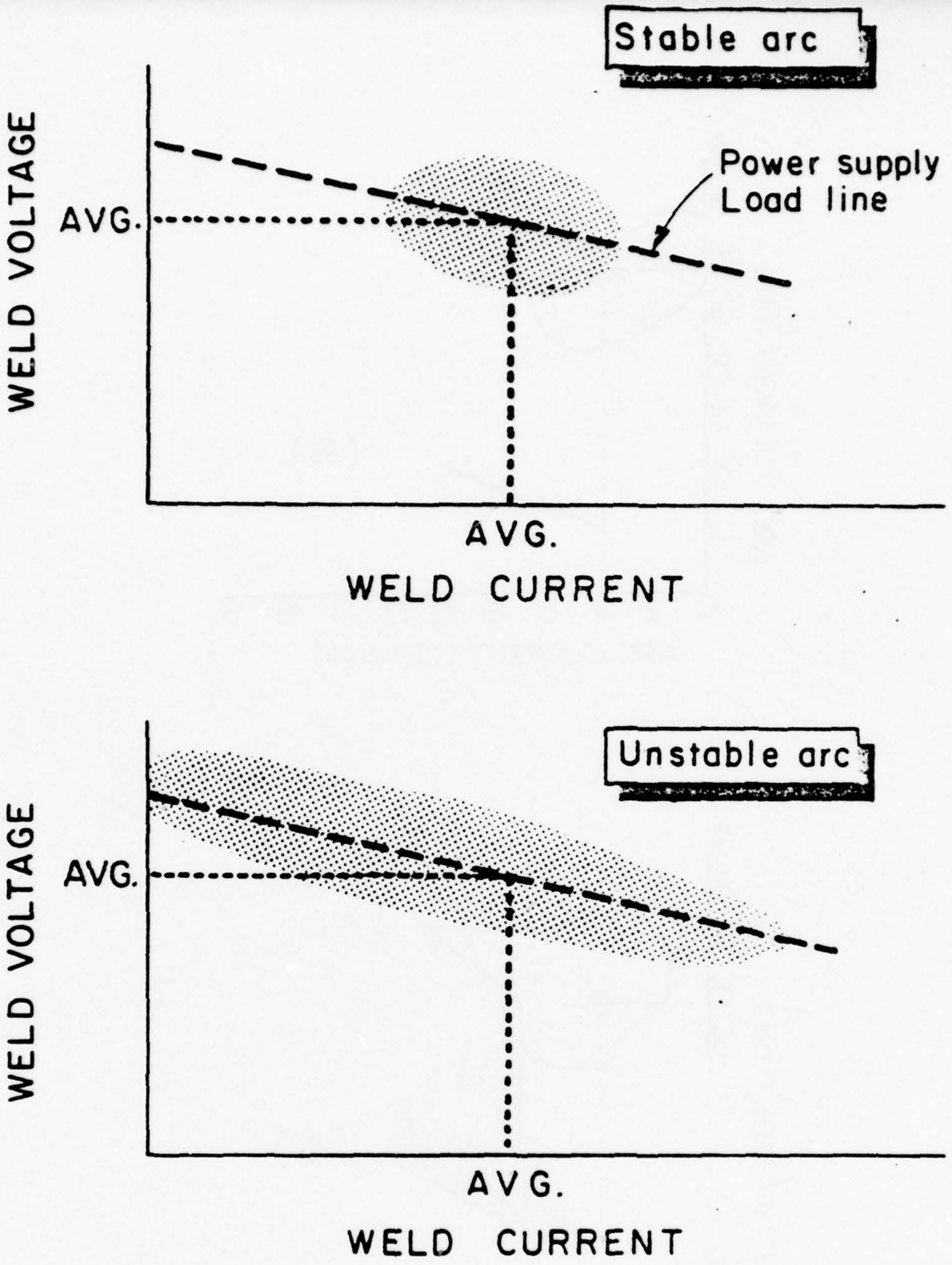


Figure 3. Schematic of arc stability measurement technique used in this study. The dynamic response of current and voltage is time averaged on a storage oscilloscope to produce a region outlining the extremes of the current and voltage fluctuations. Top--stable arc; Bottom--unstable arc intersecting the origin, indicating periods when the arc is extinguished.

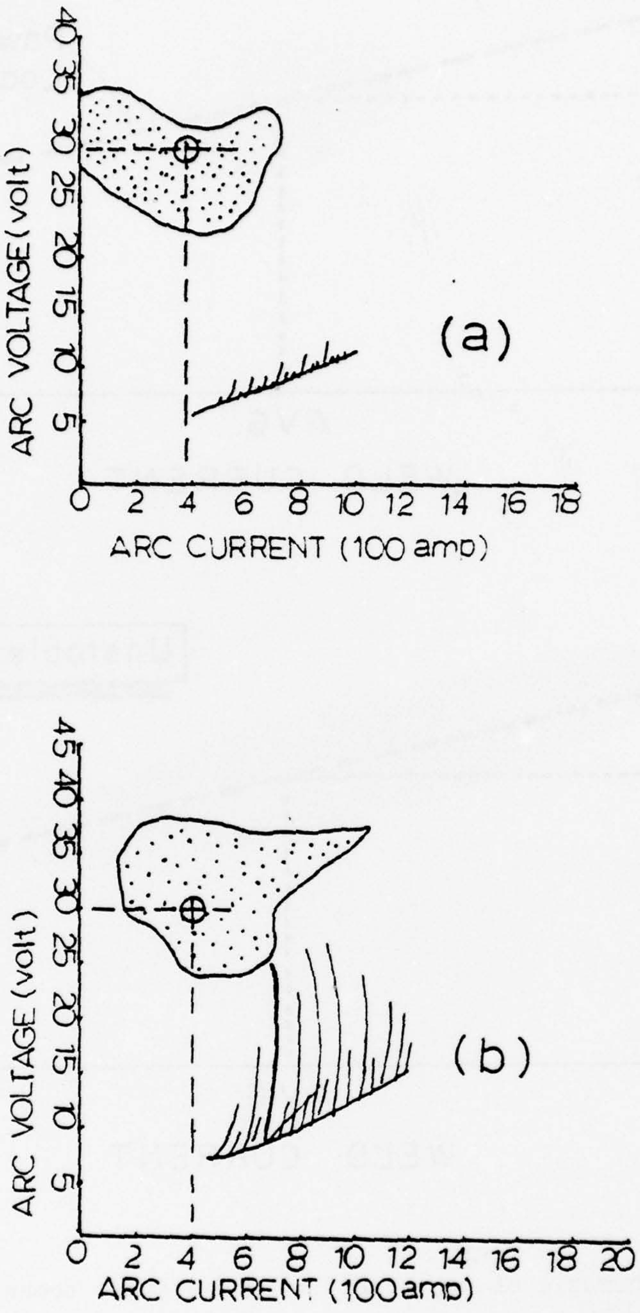
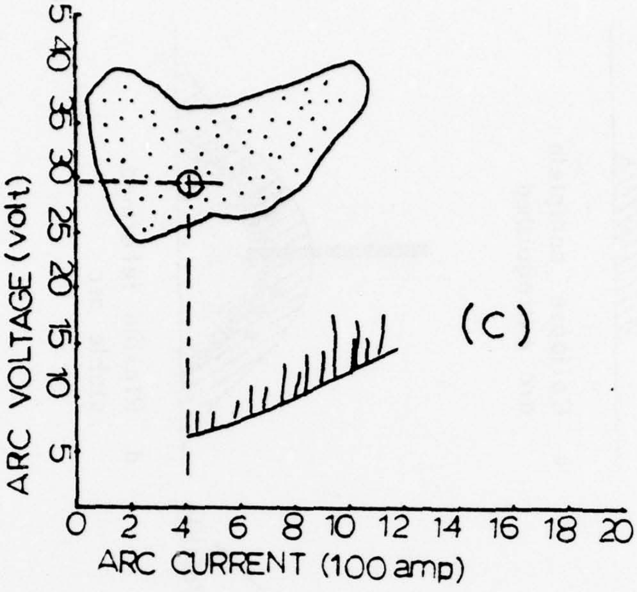


Figure 4. Arc stability traces for titanium submerged arc welds using a) optical quality CaF_2, b) CaF_2 - 1% CaO, c) CaF_2 - 1% NaF, and d) CaF_2 - 1% CaO - 1% NaF



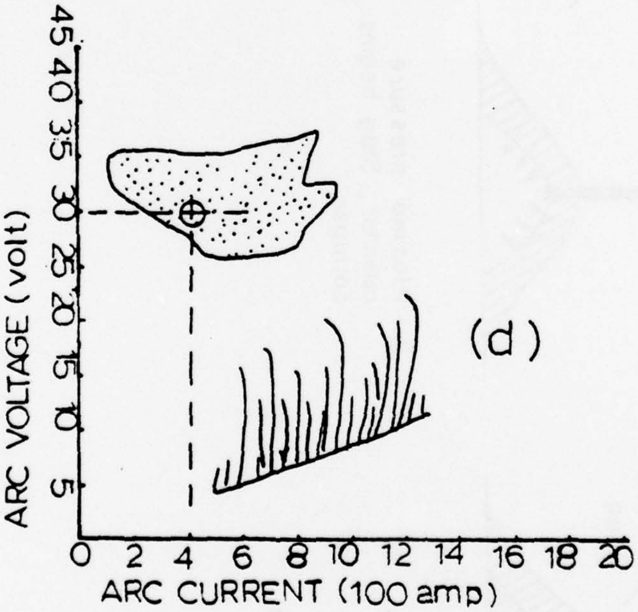
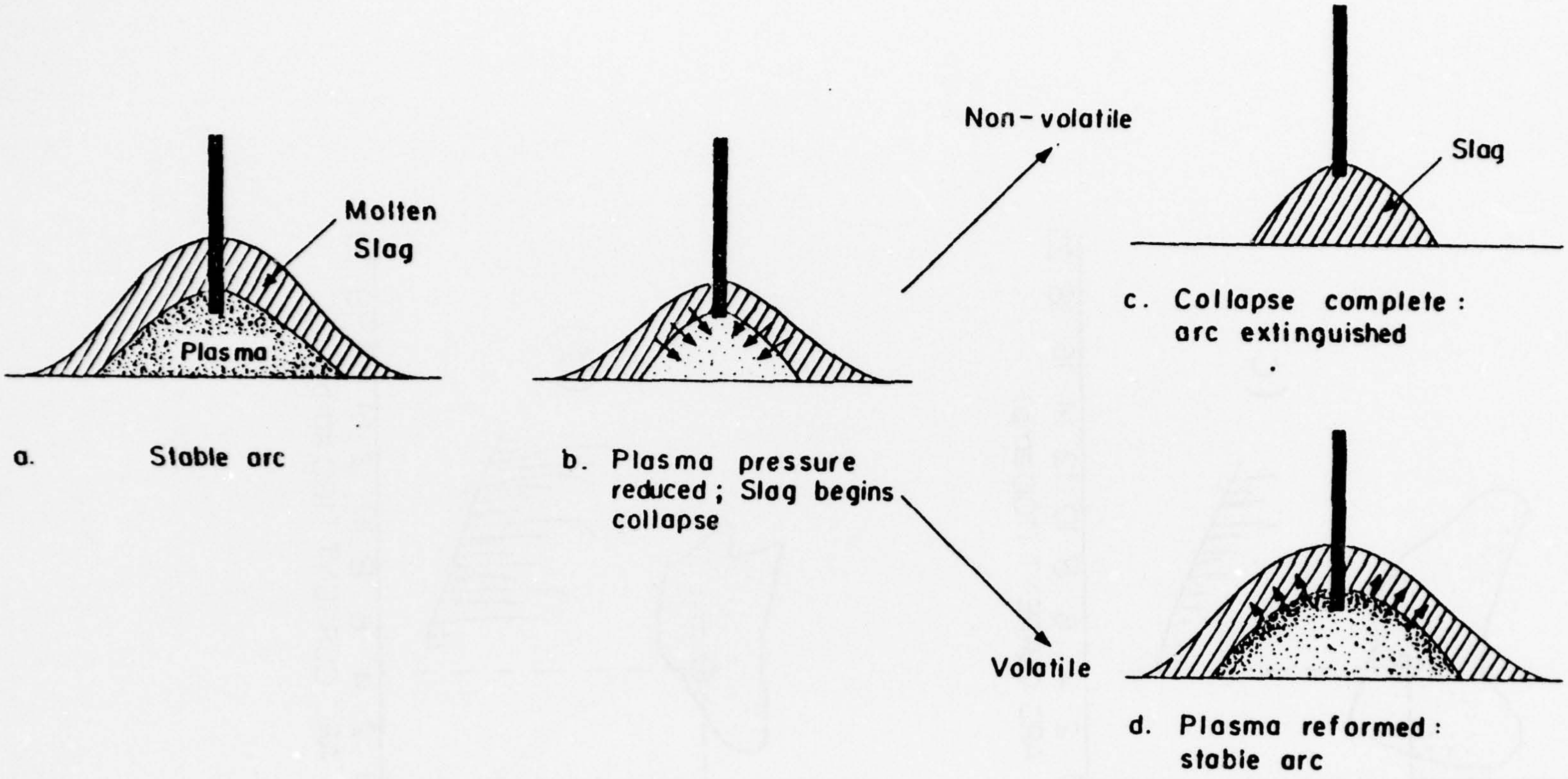


Figure 4 (cont.)



a. Stable arc

b. Plasma pressure reduced; Slag begins collapse

c. Collapse complete: arc extinguished

d. Plasma reformed: stable arc

Figure 5. Schematic diagram of the effect of volatile subspecies on the stability of submerged arc welds. Note that condition *c*) would produce the purely resistive voltage-current trace observed in titanium submerged arc welds.

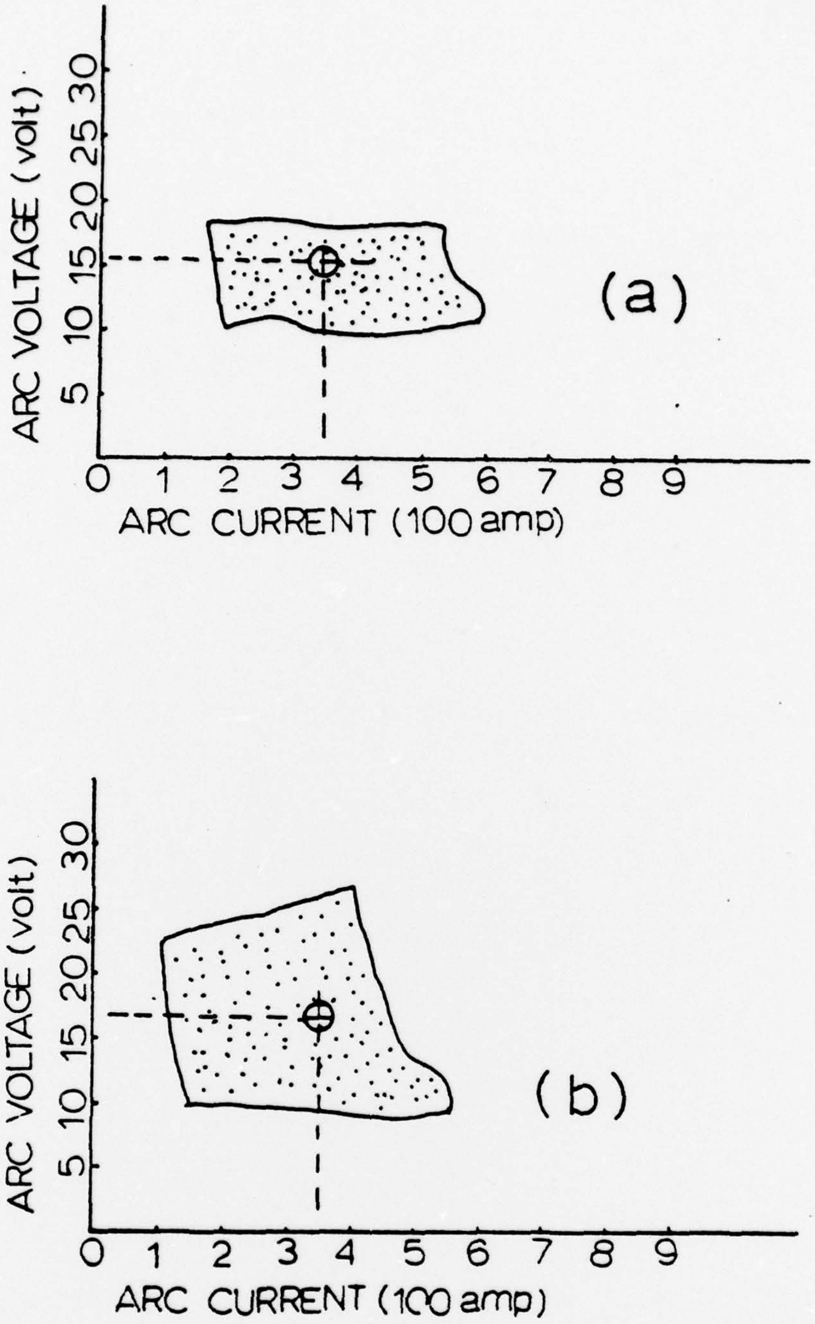
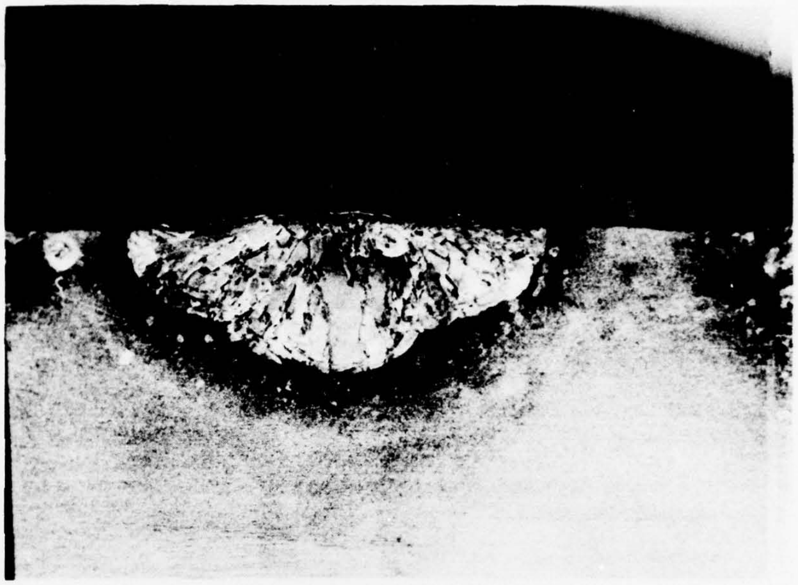
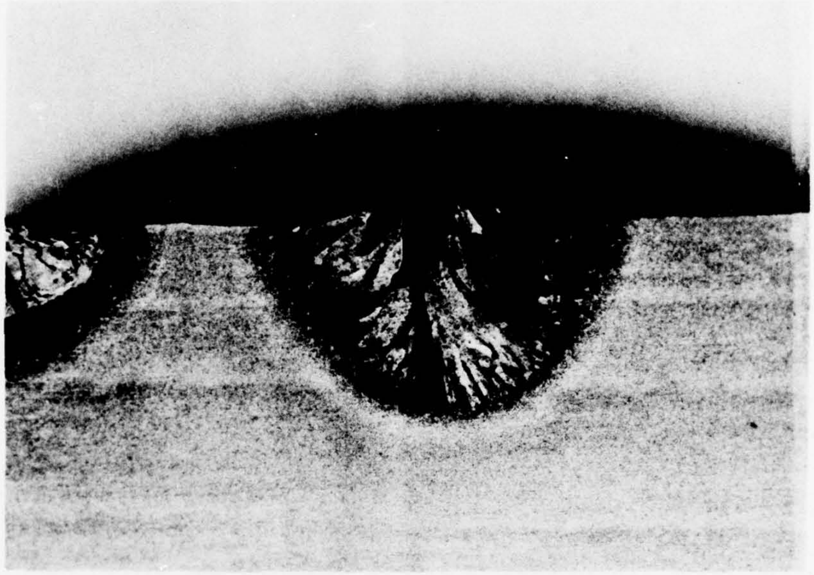


Figure 6. Arc stability traces produces with an argon shielded, non-consumable tungsten electrode. a) without CaF_2 flux and b) with CaF_2 flux.

Figure 7. Cross section of titanium submerged arc weld made with optical quality CaF_2 flux, 30 volts, 340A, 6.5 mm/sec travel. (6x)



a)



b)

Figure 8. Titanium gas tungsten arc welds made at 17 volts and 350 amps. a) without CaF_2 flux, b) with CaF_2 flux. Note the narrower deeper weld made with the flux present.

APPENDIX

Soviet Titanium Submerged Arc Welding Fluxes

The first announcement of submerged arc welding of titanium in the USSR was made in 1956 by Gurevich[1], although no information on the flux composition was given until the early 1960s. In a 1957 paper[2] and subsequently[3] Gurevich has outlined the requirements of titanium fluxes, viz.,

i) the ability to protect the liquid metal from atmospheric contamination,

ii) the ability to reduce impurities in the metal chemically, and

iii) a high melting and boiling temperature.

These requirements are generally met by the alkaline earth fluorides: Ca, Sr, Ba, and Mg, although Gurevich points out that welding qualities such as arc stability, bead appearance and absence of porosity, slag inclusions and cracks are improved by the addition of chloride salts.[3,4] In general, CaF_2 has the best properties[5], with SrF_2 and BaF_2 following; MgF_2 is omitted from the list. It is not clear whether this omission is intentional or unintentional. MgF_2 does have a much higher vapor pressure than the other alkaline earth fluorides, which may lead to excessive fuming.[6] BaF_2 has a density close to that of liquid titanium, which may result in slag entrapment[4]; hence, the earliest titanium fluxes were based upon CaF_2 and SrF_2.[7] In fact, the second flux to be classified, AN-T2, is composed solely of CaF_2.[5]

Gurevich states that different fluxes have been developed for varying thicknesses of plate; viz., "AN-T1 and AN-T3 (for up to 5 - 7 mm thick titanium) and AN-T5 and AN-T7 (for more than 7 mm thick titanium)."[3] Since other indications suggest that AN-T1 and AN-T3 are chloride free[7], while AN-T5, AN-T7 and AN-T11[4] presumably contain chlorides,* it may be that the addition of chlorides permits higher operating currents than fluxes based solely on fluorides. Nonetheless, there are several examples in the literature where thin plate fluxes are used for joining thick plate and vice versa[8,9,10]; hence, the fundamental nature of this requirement of various fluxes for varying thicknesses is questionable.

A further requirement of the fluoride-chloride fluxes described by Gurevich is that they be "oxide-free." It was not clear initially exactly how pure these fluxes were required to be. Although chemically pure ("ch" grade) and analytically pure ("ch d a" grade)[4,9,12] starting materials were used, it was found that certain lots of "pure" material produced unacceptable welds (arc instabilities, metal expulsion, and poor bead shape). It was found that either 0.5% CaO or 2% SiO_2 in the CaF_2 could cause these problems, although up to 2% Al_2O_3 had no noticeable effect. Various batches of "pure" CaF_2 which did not perform well were shown to regain their usefulness after further purification with NH_4F.[12]

One of the reasons that CaF_2 often contains significant quantities (>0.5%) of CaO is its strong affinity for moisture, i.e., the reaction

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* The rationale for assuming AN-T5 and AN-T7 contain chlorides is based upon several evidences:

i) The strong statements by Gurevich that fluxes perform better when "some fluorides are replaced by chlorides,"[3,4] would lead one to assume that at least some of the AN-T fluxes contain chlorides. Since AN-T2 does not contain chlorides[5] and AN-T1, AN-T3, and AN-T4 probably do not either[7], it is logical to assume that the later fluxes contained chlorides.

ii) Data are given which indicate that flux AN-T5 is much more hygroscopic than AN-T1 or AN-T3.[4] Since it is well known that chlorides are much more hygroscopic than fluorides, it is likely that flux AN-T5 contains chlorides. Flux AN-T7 is less hygroscopic than AN-T1 or AN-T3[4], although it is still possible that it contains chlorides as well, since non-hygroscopic fluoride-chloride mixtures may be prepared.[4,11]

$$CaF_2 + H_2O \rightarrow CaO + 2HF\uparrow$$

is very favorable thermodynamically. Although the alkaline earth fluorides are not generally hygroscopic[4,7,13], up to one per cent moisture may be absorbed on the surface of the powdered flux, leading to formation of oxides on subsequent fusion. This leads to problems in storage of the commercial titanium fluxes. To quote a Soviet article:

> Experience in the industrial use of AN-T1 and AN-T3 fluxes has shown that they are not hygroscopic. If they are stored for long periods in the open air, however, a fine layer of moisture may collect around the surface of the grain and *in this state the fluxes cannot be used for welding.* The flux was therefore supplied to the welders in cases with tightly fitting covers, and was not used for more than one shift after being roasted. At the end of this period, the flux was re-roasted.[8] (Italics added.)

Almost any titanium flux containing chlorides is hygroscopic[4,11,13], yet the beneficial effect of chloride additions has previously been noted. These conflicting requirements led to the development of flux AN-T11, a non-hygroscopic, chloride containing flux.[4]

The need for a flux which is chemically reducing is not generally met by either CaF_2 or SrF_2. Gurevich did find, however, that up to 40% LaF_3 produced a refining effect on the weld metal. The oxygen content was reduced from 1600 ppm to 1000 ppm by 40% LaF_3 in flux AN-T7[9]; however, the expense of LaF_3 may prohibit its use in anything other than an academic study.

It has been suggested that a strong impetus for the development of titanium submerged arc welding in the USSR was the unavailability of high purity argon in the mid-1950s.[14] This is confirmed by reports of the inability to remelt titanium without fluxes due to impure inert gases.[5] Nonetheless, when pure argon became available in the early 1960s[14,15], the Soviets quickly converted to what they call semi-submerged arc welding.[15]

The semi-submerged arc process is not a submerged arc process at all. It is essentially a gas tungsten arc weld in which a thin layer (.20 to .25 mm)[15] of fluoride salt paste (powder mixed with alcohol[7]) is applied to the joint prior to welding. The thickness of this layer is critical.[15,16] This thin paste causes constriction of the arc, increased penetration, elimination of undercutting, and a reduction in the net weld heat input of up to 50%.[3,7,15-18] These paste fluxes are designated AN-TA, with the A indicating the use of argon shielding gas in conjunction with the flux.[16] These fluxes may contain, but need not contain, any chlorides.[7,15,17] An example of the increased penetration caused by this flux compared with a flux-free weld is shown in Figure 1A. It was found that approximately 20% of an alkali halide must be added to the alkaline earth halides in order to achieve this effect.[15] Essentially, all alkali and alkaline earth fluorides produce this increased penetration, although some are more effective than others.[6,17] Current Soviet research is aimed at understanding the cause of this change in weld penetration[6,17], which has also been observed in the welding of niobium, molybdenum, and austenitic stainless steels.[15]

It would appear that the development of titanium submerged arc welding fluxes in the USSR was driven by an inability to produce argon of sufficient purity for either GMA or GTA welding; however, once high purity argon became available, a switch was made to the semi-submerged arc process (which is the gas tungsten arc process using a paste flux). The high cost of the very pure alkali and alkaline earth fluorides indicates that argon shielded welding is probably more economical than flux shielded welding of titanium. Nonetheless, small amounts of the inorganic salts, applied as a paste to the joint prior to welding, significantly improve the characteristics of the gas shielded welding process.

To conclude, a critical review of the literature on submerged arc welding of titanium permits the following inferences:

1) In the USSR, the development of titanium fluxes was driven by the lack of availability of high purity argon in the 1950s. With the advent of high purity inert gases, the Soviets have apparently switched to a hybrid process consisting of welding titanium with an argon shielded tungsten arc and using a very thin layer of flux to alter the arc characteristics.

2) The fully submerged arc welding process, although technically feasible, is probably economically unsound given the availability of low cost,high purity argon shielding gas.

3) The alkali and alkaline earth fluorides used in the titanium fluxes must be of very high purity and must be protected from even modest amounts of moisture contamination. This latter requirement imposes a difficult quality control restriction on the commercial utilization of these fluxes.

4) Almost any combination of alkali and alkaline earth halides is capable of fluxing welds in titanium, provided the bulk of the flux is CaF_2 or SrF_2 based and is oxide and moisture free.

5) Although it is claimed that the joint preparation for fully submerged arc welding of thick titanium plate should use either a 10-15° vee or a "U" joint[3], actual practice suggests that a very wide bevel angle is more useful.[10,19] This is likely due to a poor contact angle between the weld bead and the plate when submerged arc welding titanium.[13]

A listing of current knowledge of the compositions of the Soviet titanium fluxes is given in Table 1A.

REFERENCES

1. S. M. Gurevich and S. V. Mischenki, "Automatic Electroarc Welding of Titanium," Avt. Svarka, No. 5, 1956, p. 1.

2. S. M. Gurevich, "Certain Characteristics of Welding Titanium under Flux," Avt. Svarka, No. 5, 1957, p. 38.

3. S. M. Gurevich, V. N. Zamkov, and N. A. Kushnirenko, "Metallurgical and Technological Features of Titanium Alloy Welding When Using Fluxes," in Titanium Science and Technology, R. I. Jaffee and H. M. Burtee, eds., Plenum Press, AIME, 1973, p. 541.

4. L. K. Bosak and S. M. Gurevich, "A Non-Hygroscopic Flux for Welding Titanium and Its Alloys," Avt. Svarka, No. 5, 1966, p. 70-71.

5. S. M. Gurevich, V. P. Didkovskii, and Yu. K. Novikov, "The Electroslag Melting of Titanium Alloy Ingots," Avt. Svarka, No. 10, 1963, p. 37-42.

6. V. N. Zamkov, V. P. Prilutskii, and S. M. Gurevich, "The Effects of the Composition of the Flux on the Process of Welding Titanium with a Non-Consumable Electrode," Avt. Svarka, No. 4, 1977, p. 22-26.

7. F. R. Kulikov and V. N. Zamkov, "The Use of Oxygen-Free Fluxes for Fusion Welding Titanium Alloys," Avt. Svarka, No. 4, 1968, p. 9-12.

8. V. B. Volkov and O. A. Maslyukov, "The Submerged Arc Welding of Components Made of OT4 Titanium Alloy," Avt. Svarka, No. 10, 1963, p. 33-36.

9. S. M. Gurevich, V. N. Zamkov, S. D. Zagrebenyuk, and N. A. Kushnirenko, "The Effects of Fluxes Containing Rare Earth Elements on the Structure and Properties of Welds in VT15 Alloy," Avt.Svarka, No. 4, 1964, pp. 93-94.

10. S. M. Gurevich and V. E. Blashchuk, "Problems in the Automatic Submerged Arc Welding of the AT3 Titanium Alloy," Avt. Svarka, No. 6, 1964, pp. 24-28.

11. H. F. Petsch, "Research Study to Develop a Submerged Arc Automatic Welding Process for Fabricating Butt Welds in Thick Titanium Alloy Plate," Final Report, Contract No. N00140-68-C-0148, General Dynamics Corporation, Electric Boat Division, Groton, CT.

12. S. M. Gurevich and L. K. Bosak, "The Effects of Calcium Fluoride in Type AN-T Fluxes on Their Technical Properties," Avt. Svarka, No. 11, 1964, pp. 47-50.

13. D. C. Hill and C. L. Choi, "A Study of the Submerged Arc Welding of Titanium," Welding Journal, June 1976, p. 152-s.

14. H. W. Mishler, "A Review of Available Information on the Welding of Thick Titanium Plate in the USSR," DMIC Memorandum 188, March 6, 1964.

15. S. M. Gurevich, V. N. Zamkov, and N. A. Kushnirenko, "Improving the Penetration of Titanium Alloys When They are Welded by Argon Tungsten Arc Process," Avt. Svarka, No. 9, 1965, pp. 1-4.

16. V. N. Zamkov and V. P. Prilutskii, "Making the Penetration of Titanium More Effective in Tungsten Arc Welding," Avt. Svarka, No. 8, 1967, p. 75.

17. V. N. Zamkov, V. P. Prilutskii, and S. M. Gurevich, "The Effective Ionization Potential of the Arc When Titanium is Welded by the Semi-Submerged Arc Process," Avt. Svarka, No. 1, 1977, pp. 13-15.

18. S. M. Gurevich and V. N. Zamkov, "Welding Titanium with a Non-Consumable Electrode Using Fluxes," Avt. Svarka, No. 12, 1966, p. 13-16.

19. S. M. Gurevich, "Flux for Welding Titanium and Its Allys," U. S. Patent 3,551,218, December 29, 1970.

20. S. M. Gurevich, V. N. Zamkov, V. P. Prilutskii, V. F. Topolsky, N. V. Podkopai, S. A. Manoilo, and N. L. Dykhno, "Flux for Welding Refractory and Non-Ferrous Metals," U. S. Patent 3,849,211, November 19, 1974.

21. E. M. Levin, C. R. Robbins, and H. F. McMurdie, Phase Diagrams for Ceramists, 1969 Supplement,American Ceramic Society, Columbus, Ohio, 1969.

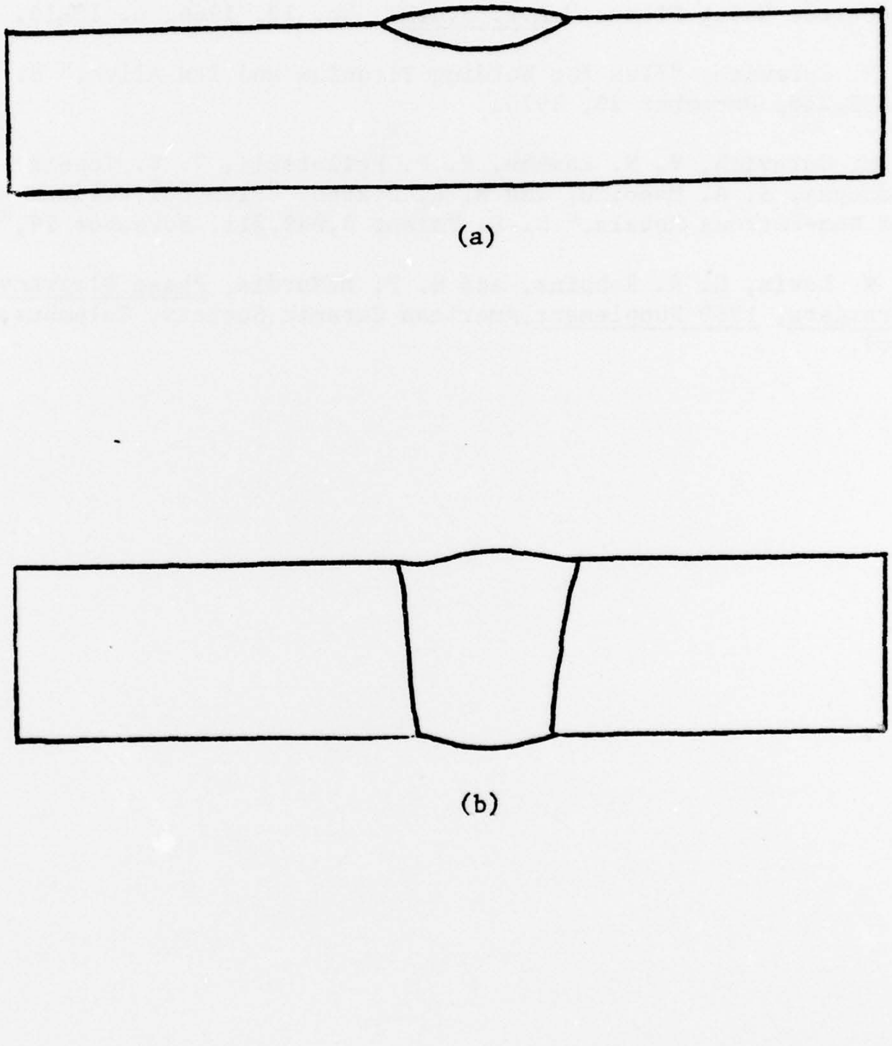

Figure 1A. Cross sections of welds made by the argon gas tungsten arc process with and without flux AN-T9A, 3.5 mm thickness, (a) without flux, (b) with flux.[15]

Table 1A. Soviet Titanium Fluxes

Flux Designation	Probable Composition	Intended Plate Thickness	Comments
AN-T1	CaF_2-LiF base[7]	3-8mm[8] 5-7mm[3]	---
AN-T2	pure CaF_2[5]	---	Higher melting and boiling temperature than AN-T1.[14] CaF_2-LiF base.[7] Used for electroslag welding.[14]
AN-T3	SrF_2-LiF base[7]	5-7mm[3]	Used for 10-25mm plate.[8]
AN-T4	SrF_2-LiF eutectic[7]	---	---
AN-T5	---	> 7mm[3]	Probably contains chlorides (see footnote in text). More hygroscopic than AN-T1 or AN-T3.[4]
AN-T7	---	> 7mm[3]	Less hygroscopic than AN-T1 or AN-T3.[4]
AN-T9A**	---	---	Paste flux.[18] May contain chlorides.[7]
AN-T11	93%[CaF_2-1%NaF] + 7%[SrF_2·$SrCl_2$] †	---	Used on 10mm thick.[4] Non-hygroscopic.[4]
AN-T13			No reference found.
AN-T15A**	SrF_2-LiF eutectic[7]*	< 6mm[7]	---
AN-T17A**	---	> 7mm(?)[3]	---
AN-T19A	---	---	---
US Patent 3,551,218[19]	77.5-94.5% CaF_2 0.5-1.5% NaF 5.0-21.0% $BaCl_2$	---	Probably very hygroscopic.[11] NaF reacts with weld metal.[19]
US Patent 3,849,211[20]	83-92% CaF_2 3-7% BaF_2 5-10% AlF_3	---	Probably not hygroscopic.
USSR Inventor's Certificate No. 348314[20]	58-66% CaF_2 34-42% AlF_3	---	Slag strongly bonded to weld metal.[20]

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* The SrF_2-LiF eutectic is approximately 65% SrF_2 - 35% LiF.[21]

** The AN-T A fluxes are paste fluxes used with tungsten electrodes and argon shielding gas.

† This flux consists of fused CaF_2 - 1% NaF and fused SrF_2 · $SrCl_2$, blended together.