INFLUENCE OF "MISCHMETAL" ON THE SUBMERGED ARC WELDABILITY OF TITANIUM

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Introduction

The number of fusion welding procedures for titanium and titanium alloys is limited by the high reactivity of these materials with oxygen, nitrogen and hydrogen, elements which can be dissolved by titanium. Only such procedures which are able to protect the fusion area and the heat affected zone against these gases can be used for welding. Besides inert gas shielded welding (argon or helium arc welding) or electron beam welding (vacuum better than 10^{-2} Torr) submerged arc welding using oxygen free granulated fluxes for protecting the seam of titanium and its alloys can be successfully performed [1], [2], [3], [4], [5], [6].

Requirements for fluxes used for welding titanium

Besides the protection against the atmosphere the fluxes for the welding of titanium have to fulfill the following main requirements:

1. preventing porosity
2. producing an easily removable slag
3. maintaining a stable arc

The suitable fluxes consist of a mixture of CaF_2 with other fluorides and chlorides. Such fluxes are:

- CaF_2 + 15 % $BaCl_2$ + 15 % NaF [1]
- CaF_2 + (5-20 %) $BaCl_2$ + (1-5 %) NaCl + (0,5-1,5 %) NaF [3]
- CaF_2 + 5 % $BaCl_2$ + 2 % LiF [4]
- CaF_2 + 5 % $SrF_2 \cdot SrCl_2$ [5]
- CaF_2 + 10 % $SrCl_2$ + 3 % LiCl [6]

It was shown, that gas is adsorpted at the surface of the granulated particles. This gas can be dissolved during the welding procedure in titanium, whereby the hardness of the fusion area and of the heat affected zone increases. The surface area of a fine flux can adsorp a higher amount of gases than the surface of a coarse flux. Therefore after welding the hardness of the seam and heat affected zone welded with a fine powdered flux is increased compared with the seam and heat affected zone welded with a coarse granulated flux. Fig.1 shows this effect with a flux of the composition 70 % CaF_2 + 15 % $BaCl_2$ + 15 % NaF [7].

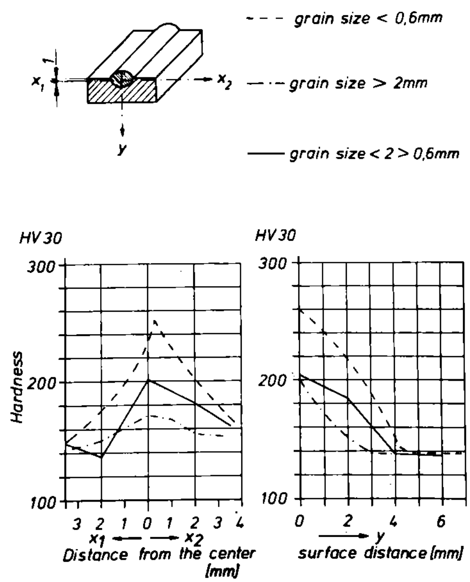

Fig. 1 Influence of granulate grain size on the hardness of the fusion zone of submerged arc welded titanium (flux 70 % CaF_2; 15 % NaF; 15 % $BaCl_2$) [7]

In order to suppress the adsorption of gases during welding it was tried to use an auxiliary argon shielding for the welding of TiAl6V4. By this argon shielding the nitrogen content in the fusion zone was decreased to 65 ppm compared with 225 ppm without argon shielding. An improved fracture toughness (K_{IC} increased from 410 to 690 $N\sqrt{mm}/mm^2$) was achieved [4]. By the following work it should be tried to dissolve the adsorpted gases of the granulated flux by an addition of "mischmetal" containing cerium, lanthanum and other rare earth metals which have a higher affinity to oxygen, nitrogen and hydrogen than titanium.

Experimental Procedure

To investigate the influence of "mischmetal" either additions of these rare elements to the welding wire or below the welding fluxes were used. Bead on plate welds were performed by welding one layer of 6 mm diameter and 500 - 750 mm length with a wire of commercially pure titanium (2 mm diameter; 0,08 wt % O) on a 15 mm thick baseplate of commercially pure titanium (0,12 wt % O). The chemical composition and the mechanical properties of both materials are given in Table 1.

Table 1
Chemical composition and mechanical properties of the baseplate and of the welding wire

	O	N	H	C	Fe		
baseplate	0,12	< 0,02	< 0,013	0,05	0,12		
wire	0,08	0,014	< 0,013	0,05	0,15		
	R_m (N/mm^2)		$R_{p0,2}$ (N/mm^2)		A(%)	Z(%)	HV
baseplate	425		314		22	35	150
wire	370		220		-	-	120

A further wire of titanium (2 mm diameter) with 0,3 wt % "mischmetal" was produced by melting titanium and "mischmetal" in an arc furnace, hot swaging of the ingots in an evacuated stainless steel tube at 800 °C and cold swaging to the final diameter. Fused and granulated mixtures of CaF_2 + 15 % K_2TiF_6 + 15 % $SrCl_2$ and CaF_2 + 5 % $SrCl_2$ with a constant particle size of 0,5 - 2 mm were used as fluxes. Preliminary investigations have shown that the fluxes containing $SrCl_2$ improve the stability of the electric arc. Particles of "mischmetal" (0,5 - 2 mm) which had a non oxidized surface, because they were kept in an evacuated glass tube, were used in another procedure. Immediately before welding these particles were put on the baseplate in the area of the intended welding seam as shown in Fig. 2.

Fig. 2 "Mischmetal" particles on the baseplate before welding

By this procedure a preliminary oxidation of the "mischmetal" was prevented. The amount of "mischmetal" was 0,2 wt % of the granulated flux. Fig. 3 shows the final state of a welded seam covered by the partially molten flux.

Fig. 3 Welded seam covered by the granulated flux

After welding a radiographic examination of the welded area was performed to detect pores. The x- and y-axes for hardness measurements from the welded seam to the baseplate and the tensile test specimen of the fusion zone for the measurement of mechanical properties are shown in Fig. 4.

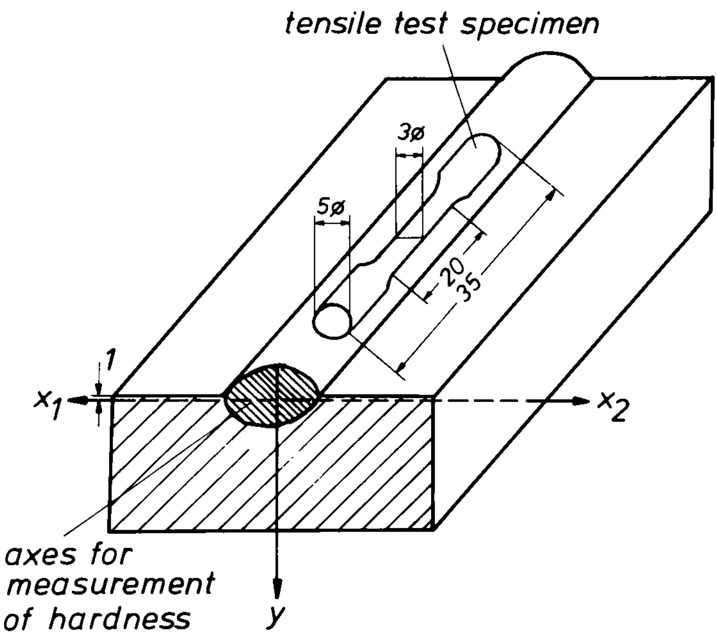

Fig. 4 Directions of hardness measurement and sample for tensile testing

Slag removal, porosity and mechanical properties of welded seams

The results in Table 2 show the characteristic selection of about one hundred bead on plate weldings with ten different variations. The flux CaF_2 + 5 % $SrCl_2$ gives a much better slag removal compared with the flux CaF_2 + 15 % K_2TiF_6 + 15 % $SrCl_2$. By the addition of "mischmetal" the slag removal is not improved, but the porosity is decreased by the "mischmetal" addition at least at a current of 210 A.

Table 2
Submerged arc welding conditions for titanium of commercial purity

Test	Flux	mischmetal content	current (A)	voltage (V)	travel speed (cm/min)	slag removal	porosity cracking
1	CaF_2 $+K_2TiF_6$ $+SrCl_2$	-	220	39	50	bad	some pores
2	CaF_2 $+K_2TiF_6$ $+SrCl_2$	0,3%(wire)	220	32	50	bad	pores cracks
3	CaF_2 $+K_2TiF_6$ $+SrCl_2$	0,2%(flux)	220	32	50	bad	some pores
4	CaF_2+SrCl_2	-	210	32	50	good	pores cracks
5	CaF_2+SrCl_2	-	210	39	50	good	some pores
6	CaF_2+SrCl_2	-	210	36	50	good	pores
7	CaF_2+SrCl_2	0,2%(flux)	210	36	50	good	no
8	CaF_2+SrCl_2	0,2%(flux)	220	36	50	good	no
9	CaF_2+SrCl_2	0,3%(wire)	210	36	50	good	some pores
10	CaF_2+SrCl_2	-	220	36	35	good	no

Fig. 5 shows the microstructure of a sample with a void in the transition region between the baseplate to the welded metal (welding speed 50 cm/min, current 210 A, voltage 32 V). A crack in the same sample is shown in Fig. 6. In the region of the welded zone cracking occurs, because the high travel speed produces a high cooling rate and residual stresses high enough for cracking. Fig. 7 shows the welded zone of a sample without pores and cracks (welding speed 35 cm/min, current 210 A, voltage 36 V). A grain growth of the transformated β-phase can be observed mainly in the direction of the heat dissipation. With increasing welding heat (higher current and voltage, lower welding speed) the grain growth is more pronounced.

Fig. 5 Pore in the microstructure of bead on plate welded titanium (J = 220 A, U = 32 V, v = 50 cm/min, flux CaF_2 + K_2TiF_6 + $SrCl_2$)

Fig. 6 Crack in the microstructure of bead on plate welded titanium (J = 220 A, U = 32 V, v = 50 cm/min, flux CaF_2 + K_2TiF_6 + $SrCl_2$)

Fig. 7 Large β-grains in the microstructure of bead on plate welded titanium (J = 220 A, U = 36 V, v = 35 cm/min, flux CaF_2 + $SrCl_2$)

Table 3 shows the results of the tension tests. The welding parameters current J, voltage U and travel speed v represent the welding energy E_w. The energy E_w which is necessary to weld a layer of the length l, is given by

$$E_w = \frac{U \cdot J \cdot t}{l} \qquad (1)$$

Since the welding speed v is determined by

$$v = \frac{l}{t} \quad , \qquad (2)$$

the energy E_w can be expressed by

$$E_w = \frac{U \cdot J}{v} \qquad (3)$$

Table 3
Mechanical properties of submerged arc welded titanium

Test Nr.	R_{m} (N/mm^2)	$R_{p0,2}$ (N/mm^2)	A (%)	Z (%)	E_w ($\frac{V \cdot A \cdot min}{cm}$)
1	464	396	15,8	42	171
2^x	430	367	9,5	21	140
3^x	460	391	19,5	40	140
4	480	402	8	24	134
5	425	315	19	46	156
6	449	377	17	46	151
7^x	445	381	23	50	151
8^x	442	370	22,6	48	158
9^x	450	371	16	40	151
10	426	360	21,5	46	226
Baseplate	425	314	22	35	-

x mischmetal additions, details in Table 2

The results of the measurements of tensile strength R_m and yield stress $R_{p0,2}$ show that the values of the baseplate are lower than those of the welded zone, whereas the formability (elongation A and reduction in area Z) of the baseplate (A = 22 %, Z = 35 %) is increased by welding with the flux CaF_2 + 5 % $SrCl_2$ with high welding energy or by addition "mischmetal" below this flux. Fig. 8 shows the values of hardness HV for the weldings with CaF_2 + 15 % K_2TiF_6 + 15 % $SrCl_2$-flux. The hardness of the baseplate

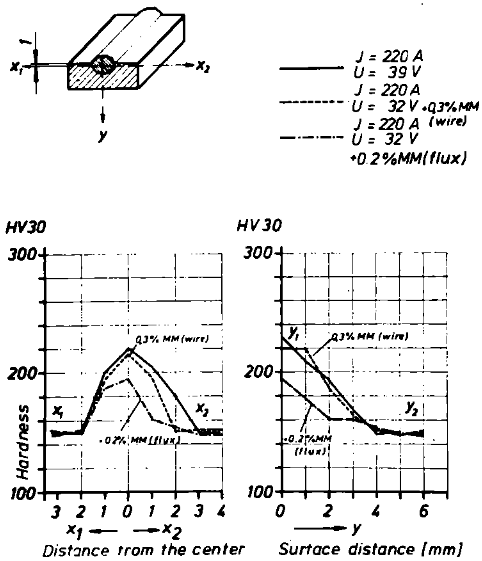

Fig. 8 Influence of "mischmetal" in wire or as addition below granulated flux on the hardness of the fusion zone of submerged arc welded titanium
wire Ø 2 mm, flux CaF_2 + 15 % K_2TiF_6 + 15 % $SrCl_2$

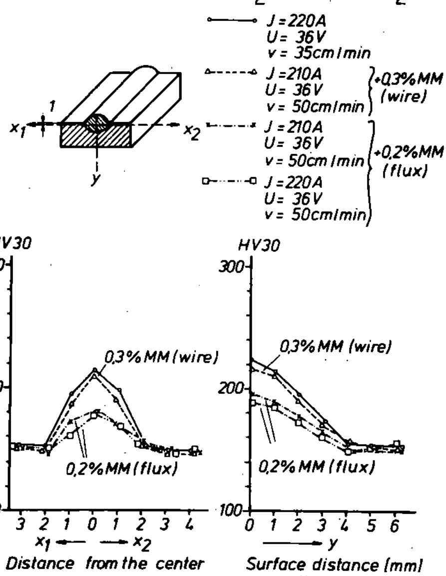

Fig. 9 Influence of "mischmetal" in wire or as addition below granulated flux on the hardness of the fusion zone of submerged arc welded titanium
wire Ø 2 mm, flux CaF_2 + 5 % $SrCl_2$

(HV 150) increases with the distance from the baseplate up to a maximum value of about HV 220. A "mischmetal" content of 0,3 wt % alloyed to the wire shows no favourable influence. The results of hardness measurement correspond to those without an addition of "mischmetal". A smaller increase of hardness can be achieved with the same flux by the addition of 0,2 wt % "mischmetal" below the flux. The maximum value of hardness amounts to 190 HV. The granulated flux CaF_2 + 5 $SrCl_2$ shows similar results (Fig. 9). The value of hardness grows to a maximum of 210 HV while by the use of the same flux containing 0,2 wt % "mischmetal" the maximum value of hardness is 180 HV.

Discussion

The decreased formability (Table 3) and increased hardness (Fig. 8 and 9) of a submerged arc welded seam of titanium compared with the baseplate arises by a reaction of the molten metal with oxygen, nitrogen and hydrogen from the air and from adsorption at the granulated welding flux. "Mischmetal" containing cerium, lanthanum and other rare earth metals is able to react with these adsorpted gases, because it has a greater affinity to oxygen, nitrogen and hydrogen. Therefore the oxygen content of the melting flux can be decreased by the molten "mischmetal", whereby the pick up of oxygen in the molten titanium via the flux will be decreased. "Mischmetal" starts melting at about 850 °C whilst the flux melts at about 1250 °C. Therefore the liquid "mischmetal" covers the surface of the titanium at a lower temperature than the flux. The amount of oxidation of the surface depends on the temperature and increases to a high degree between 850 and 1250 °C. For 50 cm seam length about 4 g "mischmetal" are used. The hardness of the welded zone of 180 HV is very low. A hardness near to this value of 195 - 205 was achieved in a former investigation by melting the fluxes at 1600 °C in a platinum crucible [2]. An addition of 0,3 wt % "mischmetal" to the welding wire corresponding to about 0,22 g for a seam length of 50 cm had no beneficial effect on the hardness and mechanical properties of the welded zone compared with submerged arc welding without this "mischmetal" addition to the welding wire. The small amount of "mischmetal" was dissolved in β- or α-Ti-solid solution. Because the melting of β-solid solution starts at about the same temperature as titanium of commercial purity (∿ 1720 °C) no reaction of the dissolved "mischmetal" with the flux can occur before the flux is molten.
Porosity takes place, if there is not enough time for solidification of the weld. By increasing the welding energy (for instance by decreasing the travel speed) the time for solidification is increased. A similar effect can be observed by the addition of "mischmetal" below the granulated flux, because the reaction of cerium and the other rare earth metals with oxygen, nitrogen and hydrogen produces additional heat by an exothermal reaction. Thus the solidification time and the time for degassing are increased. With increasing welding energy or with a "mischmetal" addition the amount of heat in the welding zone and simultaneously the grain growth of the beta phase will increase and the formability can decrease. The decrease of the formability may be small in commercially pure titanium, but it can be expected to be much larger in titanium alloys, i.e. TiAl6V4.

Conclusions

In submerged arc welding an addition of "mischmetal" (cerium, lanthanum and other rare earth metals) below the granulated flux protects the surface of the metal by melting at ∿ 850 °C and can absorp gases during the melting of the granulated flux (∿ 1250 °C). The welding wire is thus protected during the welding process by a flux having a very low oxygen content. Only a small increase of hardness from 150 HV to 180 HV is observed. The exothermal formation of heat during the oxidation of "mischmetal" increases the time for solidification of the welded zone and thus can decrease the porosity of the welded zone. Therefore the welding speed can be increased without increasing the amount of porosity.

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