

POSITION STATEMENT ON THE EFFECT OF BISMUTH ON THE ELEVATED TEMPERATURE PROPERTIES OF FLUX CORED STAINLESS STEEL WELDMENTS

BY

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1. Introduction

Many designs of modern stainless steel flux cored wires (FCW) contain a small amount of bismuth oxide (Bi_2O_3) in order to improve slag detachability and produce a clean toe line, particularly in fillet welds. These developments have been extended to cover a wide range of stainless steel compositions, including some designed particularly for elevated temperature operation, e.g. type 308H.

Unfortunately, up to about 0.02wt%Bi (200ppm) is typically transferred to the weld deposit, and there have been reports of cracking in such weldments, after a period of service. The primary cause of this cracking has been identified as bismuth in the weld metal.

This short paper reviews the published literature available and makes recommendations on the need to control bismuth in austenitic stainless steel weld metals for certain elevated temperature applications. It also summarises, in the Appendix, the results of the round robin on bismuth content in stainless steel FCW welds initiated by IIW Sub-commission IX-H.

2. Background

Although Japanese patents of 1984 (cited in ref [1]) refer to the use of bismuth oxide, the first published reference in Europe which confirmed that Bi_2O_3 was deliberately added to commercial stainless steel FCW's and resulted in reduced rupture ductility and creep strength at temperatures above 700°C (Figs. 1a and b) was at the IIW International Conference, Sweden, in 1995 [1]. This was followed in 1996 by two further Japanese papers [2, 3] which described in some detail cracking of elevated temperature components, particularly in fluidised bed catalytic cracker (FCC) units. Subsequently more systematic high temperature studies have been carried out, also in Japan, examining a range of bismuth levels in stainless steel weld metals [4, 5, 6]. Recently, work has been carried out on weld metals deposited from bismuth-free FCW's, and these have been shown to have high temperature creep properties comparable with those made with other welding processes and consumables [7].

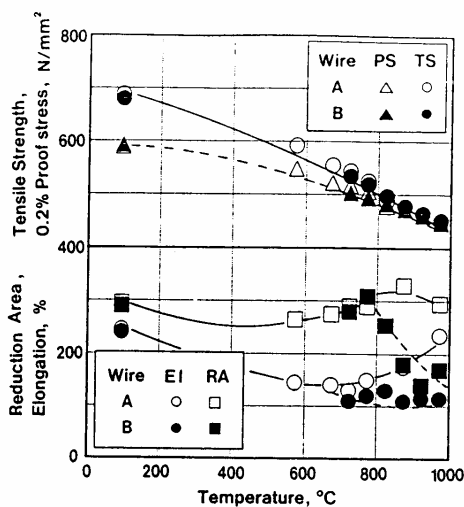


Figure 1(a) Tensile test results at elevated temperature (Wire A: $\text{Bi} < 0.001\text{wt}\%$; wire B: $\text{Bi} = 0.018\text{wt}\%$)

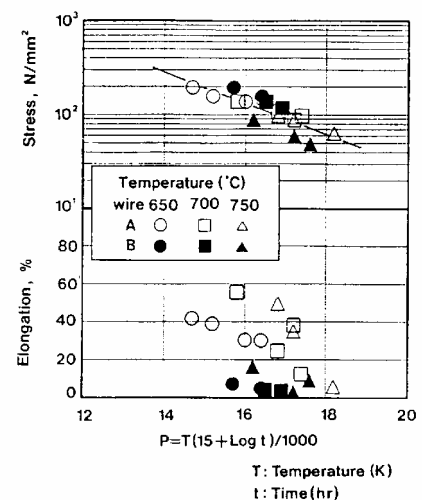


Figure 1(b) Creep rupture test results

Note that Figure 1(a) y-axis values for RofA and elongation are not correct [1].

3. Nature and Occurrence of Cracking

The Japan Welding Engineering Society carried out a most comprehensive study [1] of cracking in FCC units, particularly those which used hot-wall stainless steel components, such as flue gas lines, regenerator cyclones, catalyst standpipes, etc. Most of these components are made from 304H stainless steels, and operate mainly in the range 680-760°C. Cracks occurred in circumferential joints and attachment welds, and were detected after about 4 months of operation. The cracks were reported as initiating at the centre line of the weld deposit, and propagated interdendritically, with some branching.

In a report on a specific failure analysis [3] of a 304H separator nozzle in an FCC unit, it was noted that after one year the cracking in the FCW welds was sufficiently extensive as to cause leakage and a plant shutdown. Again, the cracking was reported as being through the weld centreline. An adjacent site weld, made using the SMAW process, showed no evidence of cracking, whereas an examination of other components in the plant, made with the FCAW process, exhibited extensive weld metal cracking.

4. Effect on Mechanical Properties

Most studies have been concerned with the effect of bismuth on elevated temperature tensile and creep properties. In the work by Nishimoto et al [5], three FCAW weld metals were investigated using hot tensile testing, covering a range of bismuth levels from nominally zero up to 410ppm (Bi ~220ppm is presented as commercial practice by all authors). In the work by Konosu et al [6] the creep performance, including creep crack growth rate, was assessed using one FCAW weld metal with 230ppm Bi and two bismuth-free weld metals (one FCAW and one SMAW deposit). Both the bismuth-free weld metals were controlled carbon (~0.06wt%) 308H types with 3-5% ferrite, whereas the bismuth-containing deposit was a low C (~0.03wt%) 308L type with a delta ferrite content of 10-11%, neither of which features are optimum for a high temperature creep resisting grade.

The results of the hot tensile testing [5] showed that bismuth had no discernible effect upon the maximum tensile strength over a range of about 500-1200°C (Fig. 2a). However, there was a clear effect of bismuth on ductility (measured as %RofA) at temperatures above about 600°C. In the range of 600°C to 1100°C bismuth-free weld metals were always exhibiting values of 50% RofA or greater, whereas the highest bismuth-containing weld metals (410ppm) showed drastic reductions down to almost zero at the higher temperatures. The intermediate bismuth level (200ppm) showed slightly improved ductility levels, but still major reductions compared with the bismuth free deposits (Fig. 2b).

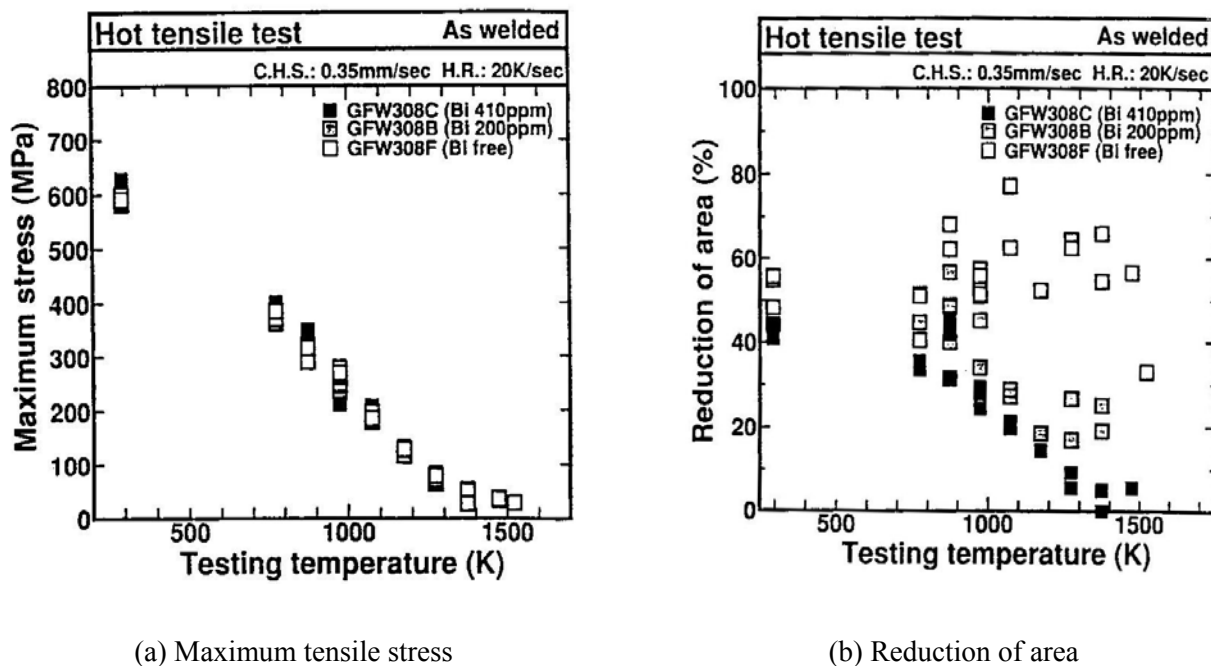


Figure 2: Hot ductility and the maximum tensile strength of Type 308 FCAW weld metals measured by hot tensile tests [5].

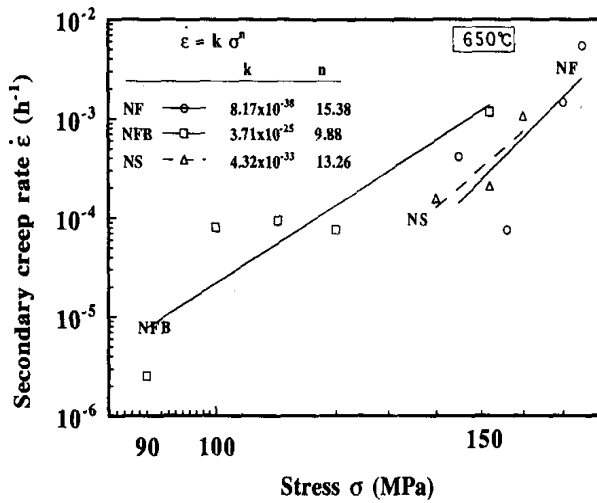


Figure 3: Secondary creep rate vs. stress (Code NFB had 230ppm Bi, the others <10ppm Bi) [6]

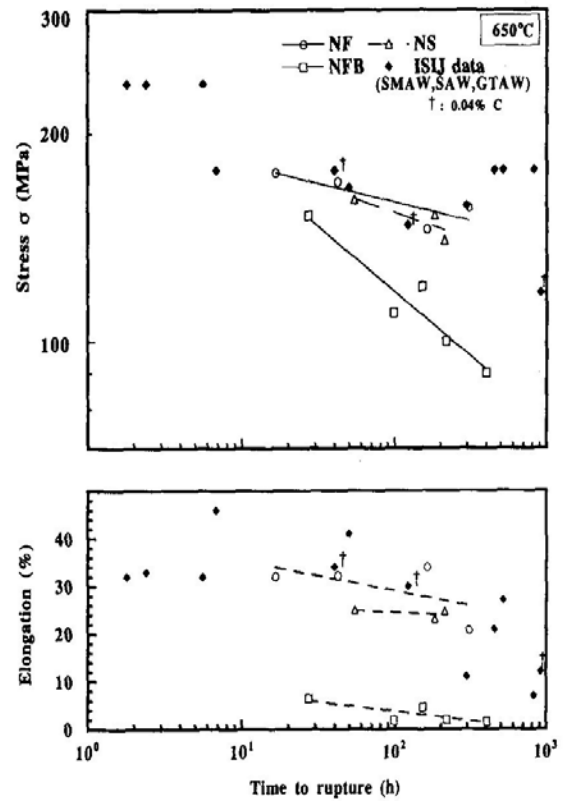


Figure 4: Creep rupture properties (Data with † marks were obtained from specimens with 0.04wt%C.) [6]

Table 1: Chemical compositions of the weld metals (wt%)

	C	Si	Mn	P	S	Cr	Ni	Mo	O	N	Bi	δ-ferrite(%)	
												Schaeffler	DeLong
NF (FCAW)	0.06	0.26	1.33	0.025	0.009	18.69	9.44	0.061	0.034	0.045	<0.001	3.5	2.8
NFB (FCAW)	0.03	0.65	1.52	0.029	0.003	20.25	10.07	0.038	0.105	0.036	0.023	10.2	11.6
NS (SMAW)	0.059	0.25	1.83	0.013	0.005	19.6	9.74	0.028	0.068	0.03	<0.001	4.7	5.6
	0.2% Proof Stress (MPa)		Tensile Stress (MPa)										
NF (FCAW)	267		691										
NFB (FCAW)	264		625										
NS (SMAW)	307		583										
JIS304 base metal	205 min.		520 min.										

The results of the creep testing [6] are shown in Figs 3 and 4. Secondary creep rate was higher, while rupture stress and rupture elongation were both greatly reduced for the bismuth-containing deposit. Even at 650°C/~280h, loss of rupture elongation was quite drastic, confirming the earlier tests shown in Fig. 1b for 308H at 650°C (shortest duration ~100h estimated from parameter). The authors noted [6] that the lower carbon in this deposit (Table 1) would have an adverse influence on creep rupture strength, but would not be expected to reduce rupture elongation. Creep crack growth rate at 650°C was also found to be much higher in this weld metal. They therefore concluded that the overriding factor in determining these properties was the bismuth content of the deposit.

More recently work by Marshall and Farrar [7] on type 300H austenitic stainless steel weld metals for high temperature service has shown that welds made with type 308H and 16.8.2 bismuth-free flux cored wires have stress rupture properties which generally exceed those of the parent materials. In addition, values are very similar to those obtained using SMAW weldments, which have a long track record of successful usage in high temperature process plant. Finally, the hot tensile ductility and stress rupture ductility properties of the two FCW weld metals were comparable with the published Japanese work obtained from bismuth-free consumables.

5. Mechanism of Cracking

The hot tensile testing of type 308 weld metal with bismuth contents of 0, 200 and 400ppm [5], carried out through a range of temperatures, showed a change in fracture appearance at about 800°C. At and above this temperature, the bismuth-containing weld metals exhibited a clear transition from microvoid coalescence to a smoother interdendritic appearance characteristic of liquation cracking.

The liquation theory is consistent with the fact that bismuth oxide has a melting point of 820°C and that bismuth has a very low solubility in the stainless steel matrix. This would suggest that bismuth oxide segregates to the grain boundaries in relatively small amounts. These grain boundary films then melt or liquate, resulting in cracking. Although no solidification cracking has been reported, the behaviour of weld metals in y-groove self-restrained hot cracking tests carried out by reheating for 1h at 800 and 900°C also showed a clear distinction between bismuth-free (no cracking) and bismuth-containing weld metals (which cracked) [5]. However, in practice, the FCC units where most of the service cracking has been reported operate in a lower temperature range of 680-760°C. It is therefore suggested that the combination of the lower temperature, stress applied over a period of time, and some partial liquation of the bismuth oxide films, resulted in microcracks which then coalesced to form larger interdendritic cracks.

In order to confirm the above hypothesis, small microcracks were introduced by tensile straining of notched Gleeble specimens at 700°C to just below failure. The specimens were then broken open in an Auger analyser to produce a “fresh” fracture surface. Analysis of this surface clearly showed the presence of bismuth. Other fractographic studies also showed the presence of bismuth on the surfaces of fractured creep specimens.

Konosu et al [6] also carried out detailed analyses of the fracture surfaces, including Auger, and stated that bismuth existed uniformly on the fracture. Bismuth segregation was found at the grain boundaries of the fracture, but it was reported that there was no sign of segregation of oxygen and they therefore concluded that elemental bismuth with a melting point of 270°C exists as a single substance at the grain boundaries to a depth of about 15Å. This is in contrast with the earlier work by Nishimoto et al [5] who suggested that the bismuth existed as bismuth oxide with a much higher melting point (820°C). Certainly the reported failures and the deterioration in mechanical testing tend to be at the higher temperatures. This, combined with the effect of bismuth on the appearance of tensile fracture surfaces, which is not visible at 700°C, whereas it is apparent at 800°C and very marked at 900°C [5], would tend to support the bismuth oxide hypothesis.

Further support for the liquation theory at higher temperatures (~750°C) is provided by Toyoda et al [4] who, in addition to carrying out tensile tests, slow strain rate tests and creep tests, examined both bismuth-containing and bismuth-free weld metals using a longitudinal Varestraint test. The specimens were prepared with a layer of FCAW weld metal, which was then remelted using the GTAW process. Very little cracking was reported using as-welded specimens (2 with and 6 without bismuth), whereas specimens which had been solution treated at 1050°C for 1 hour followed by a water quench showed a clear relationship between maximum crack length and bismuth content (Fig. 5).

These findings would suggest that bismuth activity at grain boundaries was low in the as-welded condition, but the solution treatment resulted in segregation of bismuth oxide to the grain boundaries through solid state diffusion mechanism which were then sensitive to liquation, initiation and propagation of cracks during straining in the Varestraint test.

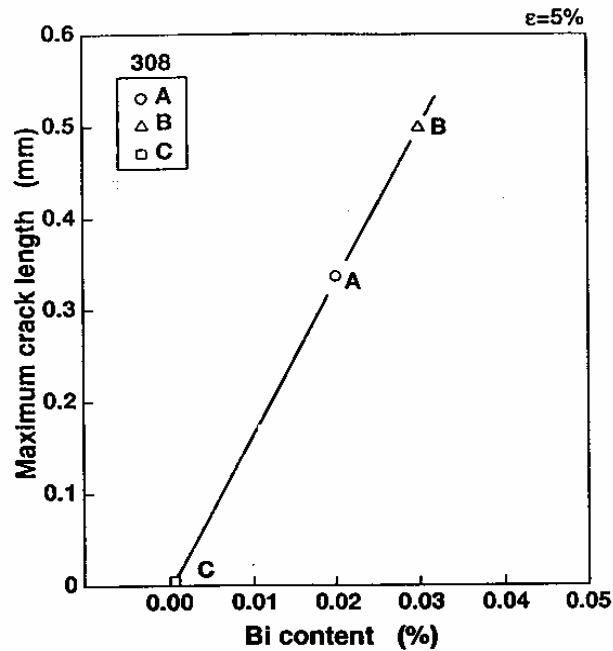


Figure 5: Maximum crack length of Varestraint testing (1050°C×1hr×WQ, HAZ of weld metal) [4]

6. Practical Implications

Once the detrimental effect of bismuth on high temperature properties had been recognised, it is understood that some end user plant operators placed a complete ban on the use of flux cored wires for certain critical applications. Subsequently there has been some relaxation of the total ban, but a recognition in at least one draft specification [8] that bismuth-containing FCAW weld metals should not be used at service temperatures above 675°C. The specification also places a limit on the ferrite to a level of 9FN maximum. However, the deleterious effect of bismuth is already evident at 650°C in short-term creep tests (Fig. 1b). In fact, a recent proposal has suggested reducing the threshold temperature to a lower level of 550°C [9]. This apparently reflects the concerns over time-dependent cracking at comparatively low temperature. The results of a y-groove self-restraint cracking test indicated that a 308H type FCAW weld metal containing 0.020wt%Bi cracked at 600°C after 10 hours and at 550°C after 100 hours (Fig. 6) [10]. However, no tests were reported beyond 100 hours and the results do not preclude failure below 550°C in the longer term.

In terms of the actual bismuth content limit, a level of less than 0.002wt% [8] or even 0.001wt% [9] has been suggested. These bismuth levels represent the maximum residual level that might be expected in bismuth-free deposits, and are about an order of magnitude less than the level of 0.01-0.02wt% typically found in bismuth-containing FCAW weld metals. In order to effectively control the bismuth level in FCAW weld metal and check the analytical accuracy of measuring Bi at various laboratories, IIW Sub-commission IX-H initiated a bismuth analysis round robin. The results are summarised in the Appendix.

The results of the Varestraint testing after solution treatment would suggest that bismuth-containing weld metal can be “sensitised” after even a relatively short period at a sufficiently high temperature, e.g. 1 hour at 1050°C. This in turn raises questions as to the potential crack sensitivity and integrity of stainless steel components welded with bismuth-bearing FCAW weld metal and subsequently solution treated. Moreover, the y-groove tests indicate that under restraint, stress-relief cracking might occur before the solution treatment temperature is reached.

This situation does not arise for the majority of stainless steel fabrications, which are normally left in the as-welded condition. However, there are cases such as fabricated pressure vessel heads, castings and some large/complex fabrications which are solution heat treated to achieve the correct microstructure

and/or dimensional stability where the possible outcome of using bismuth-bearing consumables should be assessed. This particular issue is acknowledged in the original reference to bismuth in flux cored wires [2]. Again, while $>800^{\circ}\text{C}$ poses a potential reheat cracking hazard when Bi is present, below 730°C and based on the time to onset of in-service cracking in 308H [3], there should be no problem at conventional PWHT temperatures as sometimes applied to stainless overlays or dissimilar weldments.

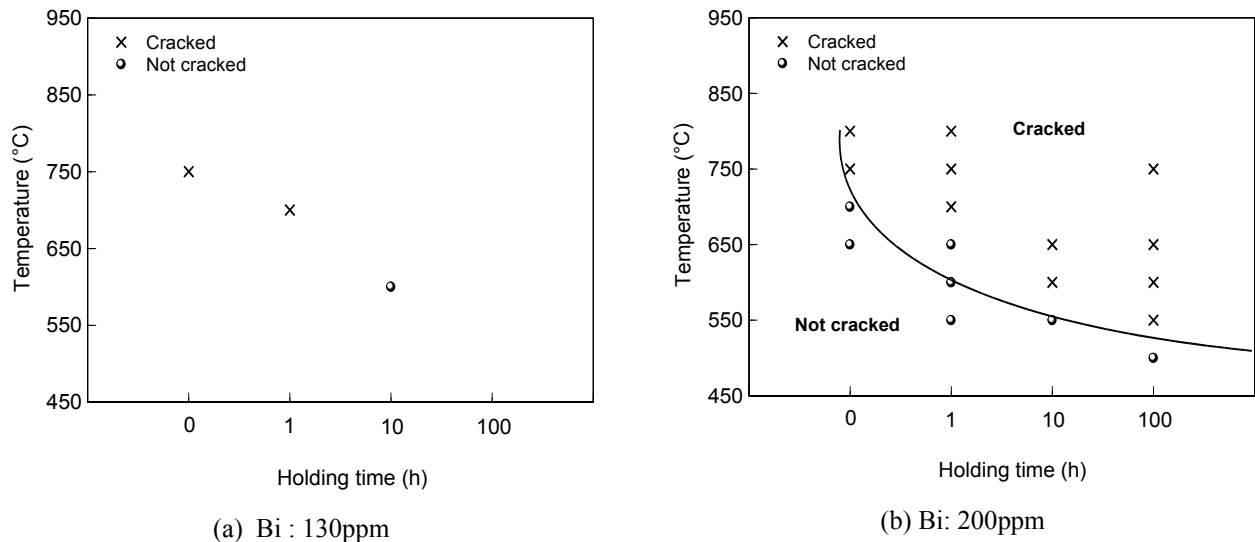


Figure 6. Results of y-groove self-restraint cracking test of Type 308H FCAW weld metals (after [10])

7. Conclusions

1. There have been reports of cracking in stainless steel fabrications operating in the range 680°C – 750°C and welded with bismuth-containing flux cored wires. Bismuth oxide is a deliberate addition to the flux system of some flux cored wires in order to improve slag removal, but consequently the weld deposit will typically contain up to around 0.02%Bi.
2. A number of workers have shown that welds made with bismuth-containing consumables have much reduced hot tensile and stress rupture ductility when compared with bismuth-free versions.
3. The exact mechanism of cracking has not been established, but is believed to arise from grain boundary films of bismuth or bismuth oxide which liquate at high temperatures.
4. It is recommended that welding consumables and, in particular, flux cored wires which are to be used in fabrications which are designed to operate at temperatures above about 550°C or are to be postweld solution heat treated (950°C – 1050°C) should have a maximum bismuth content of 0.002wt% (20ppm). However, the deleterious effect of bismuth is evident at 650°C in short term creep tests and even at as low as 550°C in y-groove tests, the latter being the lowest temperature for which time-dependant data have been reported. Similarly, the data show that bismuth could provoke stress-relief (reheat) cracking at least down to 800°C .

8. References

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Appendix

IIW ROUND ROBIN: BISMUTH IN STAINLESS STEEL FCW WELDS

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1. Background

In recognition of the detrimental effect of bismuth on high temperature properties, some authorities have recommended that, for elevated temperature applications or structures that need solution heat treatment after welding, bismuth-free welding consumables should be used. Certain threshold temperatures, such as 765°C or 550°C have been proposed. In terms of the actual bismuth limit, a level of less than 0.002wt% or even 0.001wt% has been suggested.

In order to effectively control the bismuth level in weld metal, it is essential that the welding industry, particularly welding consumable manufacturers can establish bismuth level with necessary accuracy and that different laboratories give reasonable consistency in analysis result. In order to check various laboratories, IIW Sub-commission IX-H decided to initiate a bismuth analysis round robin at its last annual meeting in The Hague. The project was organized by Metrode Products Limited.

2. The consumables

Two types of stainless steel flux cored wires were chosen for the round robin exercise. These wires were rutile type FCWs, one of which had a deliberate bismuth oxide addition whilst the other did not. The specifications and size of the wires were as follows;

FCW code	AWS specification	Size	Bismuth oxide
Wire A	E308LT0-4	Ø1.2mm	Deliberate additions
Wire B	E308HT1-4	Ø1.2mm	No additions

3. Details of the sample preparation

Two weld deposits were prepared using the following conditions;

Welding parameters:	V = 28Volts; I = 190Amps
Shielding gas:	Ar + 20%CO ₂
Shielding gas flow rate:	20l/min
Welding position:	Downhand
Bead arrangement:	Overlapped stringer beads.

Figure 1 illustrates the geometry of the test FCW weld deposits.

To suit different testing requirements, the weld deposits were machined into two sets of blocks (two of each wire), in dimensions of 40mm(wide)×55mm(long)×45mm(high), and metal chippings. They were coded as Sample A and Sample B. During the machining of the weld metal chippings, special care was taken to avoid the diluted areas between the undiluted deposit and base plate.

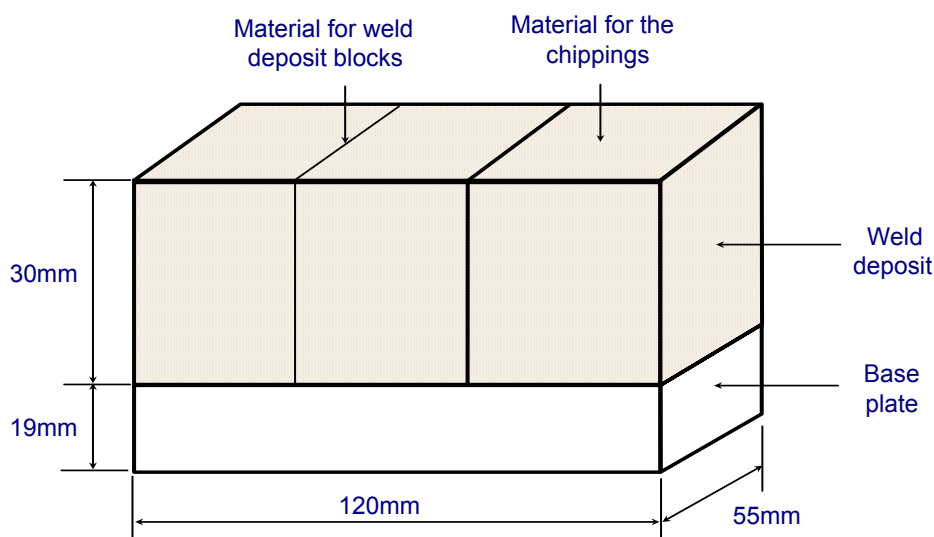


Figure 1. Geometry of the weld deposits

4. General chemical composition of the weld metals

Using optical emission spectrometry, the chemical composition of the test weld metals was analysed. The ferrite content of the deposits was measured using a Feritscope calibrated with IIW secondary standards. The results are listed in Table 1.

Table 1. Chemical composition and δ ferrite content of the weld metals (wt%)

Sample	C	Mn	Si	S	P	Cr	Ni	Mo	Cu	Al	FN
Sample A	0.031	1.51	0.71	0.0098	0.0275	19.76	10.20	0.12	0.09	0.018	9
Sample B	0.049	1.49	0.67	0.0104	0.0290	18.49	9.67	0.12	0.09	0.023	4

5. The participants

Seven IIW members from Austria, Germany, Japan, Sweden, UK and USA participated the exercise. They analysed the samples in forms of either metal chippings or solid weld blocks. Two UK based independent laboratories were also supplied with the samples and carried out analyses. These participating laboratories are coded as Lab A to Lab I.

6. The results

Results have been received from all the seven participants and two independent laboratories. Table 2 lists the test results and analytical methods that were used.

In the samples tested, wire A has a deliberate bismuth oxide addition and therefore Sample A should contain a certain level of Bi. Wire B does not have bismuth oxide addition, so the Bi in Sample B should be a trace level. The data received show that all participants with valid results identified the bismuth content difference and in the correct order. Of the laboratories, seven reported reasonably close values in a range of 124-160ppm for Sample A, the average and spread being 142 ± 18 ppm. For the nominal Bi-free Sample B, all except one laboratory reported a Bi content of 0.6 to 20ppm, which no doubt reflects the detection limit, reproducibility and any interference effects according to analytical techniques. On the basis of these results, a practical threshold limit of 0.002wt%Bi (<20ppm) seems acceptable for the

specification of “bismuth-free” weld metal. It is recognised that the actual bismuth level here may be 1ppm or lesser, as reported by four laboratories.

Two of the nine laboratories (Labs F and H) reported some Sample A values which were outliers to the above set, presumably owing to calibration difficulties, Lab F reported twice the average and Lab H less than half the average of other laboratories. Lab H also reported <50ppm for Sample B, a very high detection limit.

Table 2. The bismuth round robin results

Company	Method	Bi content in Sample A, ppm	Bi content in Sample B, ppm
LAB A	Optical emission spectrometry (OES)	127	20
LAB B	Inductively coupled plasma OES (ICP)/MS	124	<5
LAB C	Atomic absorption spectrometry (AAS)	140	5
LAB D	1. AAS (flame) (for A) 2. AAS (for B)	152	1
LAB E	AAS (furnace)	140	0.6
LAB F	AAS (furnace)	285	<10
LAB G	1. ICP (for A) 2. AAS (furnace) (for B)	150	1.01
LAB H	Hollow Cathode OES (HCS)	60	<50
LAB I	ICP/MS	160	0.6

7. Intermediate Conclusions

- a) Analyses for bismuth content have been carried out on weld deposits from two stainless steel flux cored wires – one with deliberate additions of bismuth oxide and one without.
- b) Nine laboratories from six countries have been involved in the exercise. Of these, seven laboratories gave reasonably consistent results and clearly differentiated between the high and low bismuth levels.
- c) With two exceptions, high values were 142 ± 18 ppm and low values from 0.6 to 20 ppm. On the basis of these results, a practical threshold limit of 0.002 wt% Bi (<20 ppm) seems acceptable for the specification of “bismuth-free” weld metal.

Acknowledgement

The authors were very grateful for the cooperation provided by all round robin participant laboratories.