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Short Communication

Spectrochemical Investigation of Aluminum Master Alloys

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Abstract

The objective of this study is to observe the significance of sampling fractions in spectrochemical analysis of aluminium master alloys. Aluminium master alloys are difficult to analyze by routine analytical methods due to inhomogeneity and high percentage of the alloying elements. In this study aluminium master alloys were remelted along with aluminium ingots of 99.9% purity in an electrical crucible furnace and subsequently analysis by spark optical emission spectrometer (OES). The bulk samples of a particular aluminium master alloy for re-melting process was chosen by two different methods and evaluated for % recovery of the target element. It was observed that sampling fractions and compilation techniques greatly affects the compositional results of aluminium master alloys. The 20% bulk sampling showed good recoveries and very precise results for each alloying element in the respective master alloy. The results of spark OES were cross checked by X-ray fluorescence spectrometer (XRF) with the help of certified reference materials.

Keywords: Aluminum master alloy, Spark optical emission spectrometer, X-ray fluorescence, Re-melting.

Introduction

Aluminum master alloy is aluminum combined with a relatively high percentage of one or two other elements. The use of aluminum master alloy offers distinct advantages over the addition of elemental metal during alloying [1, 2]. Three major advantages are; (a) these can be calculated to become part of the initial cold charge i.e. melted with the metal at low temperature. This rapid dissolution results in a significant reduction in dross formation, minimal gas pick-up and extended furnace life (b) significantly reduces the amount of energy required and shortens the length of melt time (c) gives higher accuracy to meet specified composition limits. Commonly used aluminum master alloys are Al-Mn, Al-Si, Al-Cu, Al-Fe, Al-Ni, Al-Cr, Al-Ti & Al-Mg, and are available in 5 kg ingot or 7 kg waffle plate form.

The stated benefits can only be attained by knowing the authentic composition and actual condition of a particular master alloy. For instance, manufacturer provides a broad composition range of a single lot of a master alloy i.e. Al-Si 50% means Si may be 47-52 % or else as affirmed by the supplier. Conversely for charge calculation one should know the nearest possible true composition of that master alloy, so that melt could be adjusted as quickly as possible to minimize the energy cost and to save time.

Spark optical emission spectrometry (OES) is an effective industrial tool for verifying melt chemistry [3]. A small sample of the molten metal alloy is drawn off from the molten bath and poured into a mold made to the ASTM specifications [4, 5]. The sample is allowed to solidify and then it is machined to find a surface that is representative of the melt and necessary for OES analysis. This sampling and machining process must be conducted on every sample drawn from melting furnace any time an addition or change is made. Machined samples are then

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subjected to spark OES following ASTM procedure [6]. Alternatively, the solid sample at room temperature may be subjected to static X-Ray fluorescence analysis [7-9]. If the sample does not fall within the specified compositional limits, adjustments are made to the liquid melt and the process must be repeated until the final composition falls within the allowable tolerance limits. Each time an addition is made, time must be allowed for convective mixing of the melt before another sample is drawn for analysis. Compositional adjustment is a time consuming process that wastes considerable energy and it can take 45 minutes to 1 hour or more.

Master alloys play an important role in the adjustment of melt composition quickly. But for this purpose we must have exact value of alloying element & level of impurities in respective master alloy. Here we presented a quick and reliable method to assess the actual condition of an aluminium master alloy stock.

Experimental

Apparatus

Spark optical emission spectrometer of OBLF Germany model QSN 750 Analyzer and X-ray fluorescence spectrometer of PANALYTICAL model MagiX was used for chemical analysis. An electrical crucible furnace of 200 kg capacity with temperature range up-to 800^{o}C was used for melting of aluminium master alloys. A lathe machine model Myford of Nottingham England was used for sample preparation.

Sampling

We employed two sampling procedures for a single lot of aluminium master alloy as described below:

Method-I (10% bulk sampling)

In this method we took one ingot/waffle plate from each pallet of the respective master alloy and covered 10% pallets of that lot randomly. From this bulk sample we selected melting sample such that 50% ingots were used as a whole without further subdivision. Remaining 50% ingots were divided into two halves, of which one portion was used in melting.

Method-II (20% bulk sampling)

In this method we took two ingots randomly from each pallet of the respective master alloy and covered 20% pallets of that lot. From this bulk sample 50% ingots were cut down into two pieces and the remaining 50% ingots were divided into four parts. Equal quantity from both proportions was used in melting.

Re-melting of aluminum master alloys

The master alloy samples taken by both procedures were re-melted one by one with commercially pure aluminum ingots of 99.9% purity. Master alloy ratio to pure aluminum was adjusted according to the equipment's linear range and availability of CRM. The crucible furnace was loaded with accurately weighed aluminum ingots. As the aluminum ingots melted properly, two samples were taken for spark OES analysis. The weight of the samples was also recorded. After that known quantity of aluminum master alloy was added and melting was completed by keeping the metallurgical conditions fulfilled.

Analytical samples

Remelted master alloy samples were collected from the furnace according to the ASTM E716-94 using B type mold [5]. The analytical samples were surfaced on a lathe machine at a constant speed. Machined samples were immediately placed in a desiccator and analyzed by spark OES [6] and XRF spectrometer [10].

Results and Discussion

In Table 1 we have tabulated the available analytical methods (ASTM) and their detection ranges for aluminum base alloys [11-14]. It is clearly evident that none of the methods fully cover the concentration ranges of aluminum master alloys, some of those are summarized in Table 2. The first two conventional methods gravimetric and titremetric are very lengthy and time consuming procedures. These methods require a separate setup, lot of chemicals and skilled labor.

Colorimetric methods cover very low ranges so they can be used only for trace elements and low range alloys [15, 16]. More importantly this technique consumes a very little sample for analysis which could not be the representative sample of the whole lot. For example a sample of 0.1-1 g will never be a representative sample of 10 ton of master alloy. Next two methods AAS and AES also do not cover the whole range of the aluminum master alloys. Similarly these two techniques require a very little sample and in solution form [17, 18]. All of the above wet chemical analysis requires a huge setup which will not be in the scope of industry in the presence of spark OES.

***Table 1*. Detection ranges (Wt. %) of ASTM methods for aluminium base alloys [11].**

Element	Gravi-metry	Titre-metry	Colori-metry	AAS*	AES**	Spark OES
Si	0.5-20		0.05-1	0.05-0.3 [17]	0.07-16	0.001-24
Cu	0.5-20		0.04-5 [15]	0.01-10	0.001-5.5	0.001-20
Mg		0.1-5		0.002-5	0.03-5.4	0.001-11
Ni			0.02-3.2 [16]	0.01-4	0.005-2.6	0.001-4
Cr			0.01-0.3	0.01-1	0.001-0.23	0.001-1
Mn			0.005-2	0.01-2	0.001-1.2	0.001-2
Ti			0.003-0.3		0.002-0.12	0.001-0.5

*AAS= atomic absorption spectrometry,
**AES= atomic emission spectrometry

***Table 2*. Al master alloys used in present study.**

Aluminium Master Alloy	Specified Conc. range (Wt. %)
Al-Si 50%	47.5 - 52.5 %
Al-Cu 50%	47.5 - 52.5 %
Al-Mg 20%	18 – 22 %
Al-Ni 20%	18 – 22 %
Al-Cr 5%	4.5 - 5.5 %
Al-Mn 10%	9.0 – 11 %
Al-Ti 10%	9.0 – 11 %

Although the spark OES and XRF techniques have a wide range for many elements still we cannot analyze the whole range of master alloys due to unavailability of such a high concentration CRMs. This was the reason, we brought down the concentration of various aluminum master alloys by dilution with pure aluminum to a degree so that these could be analyzed by spark OES. Re-melting of aluminum master alloys was performed according to standard procedures [19]. Table 3 briefly describes the methods which we adopted to collect the bulk samples for re-melting process.

***Table 3*. Summary of sampling ratios employed in present study.**

Method Name	Bulk sample	Test sample for re-melting	Analytical sample
10% sampling	1 ingot from each pallet, and 10% pallets of each lot	50% ingots used as a whole, remaining 50% ingots divided into two halves	4 samples from each melting, by ASTM method [5]
20% sampling	2 ingots from each pallets, and 20% pallets of each lot	50% ingots divided into two parts, remaining 50% ingots divided into four parts	4 samples from each melting, by ASTM method [5]

Results of 10% sampling procedure

The spark OES results of pure aluminum used for dilution purpose in first procedure named as batch-I (Table 4), which confirmed the purity level. In Table 5 results of re-melted master alloy samples analyzed by spark OES and XRF has been presented. We can see only three results fall within the supplier's range (Table 2) and these are Al-Cu, Al-Cr and Al-Mn, average values of two techniques are 49.2%, 4.63% and 9.98% respectively. The results of Al-Si (46.7%), Al-Mg (16.5%), Al-Ni (17.7%) and Al-Ti (7.73%) do not fall within the specified range. It is notable that Al-Mg is the most farthest among the deviated results; because Mg quickly oxidizes during melting [20-22] which contributes in low recovery.

***Table 4*. Spark OES results of commercially pure aluminium ingots.**

Elements	**Aluminium (Batch-I)**			**Aluminium (Batch-II)**		
	$\bar{X}$	S	C_v	$\bar{X}$	S	C_v
Si	0.034	0.0004	1.04	0.037	0.0003	0.77
Fe	0.064	0.0017	2.67	0.079	0.0007	0.90
Cu	0.001	0	5.24	0.001	0	0.0
Mn	0.001	0	0.0	0.001	0	0.0
Mg	0.001	0.0002	28.2	0.001	0.0002	24.9
Cr	0.001	0	0.0	0.001	0.0001	23.5
Ni	0.005	0	0.0	0.003	0	0.0
Zn	0.002	0	0.0	0.002	0	0.0
Ti	0.003	0	0.0	0.003	0	0.0

$\bar{X}$ =Mean, **S=**Standard deviation, C_v = Coefficient of variation

***Table 5*. Results of 10% sampling procedure.**

Aluminium Master Alloy	**Spark OES results**			**XRF analysis results**			$\frac{\bar{x}_1 + \bar{x}_2}{2}$
	$\bar{X}$	S	C_v	$\bar{X}$	S	C_v	
Al-Si 50%	47.16	0.028	0.44	46.23	0.051	0.87	46.7
Al-Cu 50%	48.02	0.071	1.87	50.29	0.005	0.13	49.2
Al-Mg 20%	16.59	0.014	0.51	16.35	0.15	0.68	16.5
Al-Ni 20%	17.32	0.032	1.65	18.00	0.28	1.59	17.7
Al-Cr 5%	4.36	0.004	1.19	4.89	0.015	4.58	4.63
Al-Mn 10%	10.04	0.001	0.06	9.91	0.005	0.43	9.98
Al-Ti 10%	7.83	0.039	11.75	7.62	0.02	6.06	7.73

Results of 20% sampling procedure

Results of 20% bulk sampling have been placed in Table 6, and these found satisfactory when compared with supplier's specification. Recovery of each element in respective master alloy is enhanced and more precise results have been obtained. The average results of the two techniques are Al-Si (48.5%), Al-Cu (48.9%), Al-Ni (18.9%), Al-Cr (5.06%), Al-Mn (9.49%) and Al-Ti (9.41%). These results clearly satisfy the specified range. Only the Al-Mg (17.7%) is little deviating, definitely due to the oxidation. Magnesium is more reactive then aluminum and diffuses easily to the surface and oxidizes. The oxide formed is not protective and therefore magnesium losses increase with increased holding time [22].

It is evident by comparing Table 5 & 6 that 20% bulk sampling improved the results of Al-Si, Al-Mg, Al-Ni and Al-Ti master alloys.

***Table 6*. Results of 20% sampling procedure.**

Aluminium Master Alloy	**Spark OES results**			**XRF analysis results**			$\frac{\bar{x}_1 + \bar{x}_2}{2}$
	$\bar{X}_1$	*S*	C_v	$\bar{X}_2$	*S*	C_v	
Al-Si 50%	48.90	0.014	0.24	48.17	0.067	1.13	48.5
Al-Cu 50%	48.95	0.000	0.0	48.83	0.115	1.44	48.9
Al-Mg 20%	17.52	0.039	0.51	17.81	0.167	2.33	17.7
Al-Ni 20%	18.54	0.055	3.22	19.22	0.021	1.05	18.9
Al-Cr 5%	5.06	0.012	1.70	5.06	0.006	0.88	5.06
Al-Mn 10%	9.66	0.026	1.42	9.31	0.01	2.17	9.49
Al-Ti 10%	9.46	0.034	6.86	9.36	0.03	1.69	9.41

Conclusion

Compositional analysis of aluminium master alloys can be performed quickly and effectively by Spark OES after dilution with pure aluminium. This study showed that extensive and systematic sampling is required for good results. The results of 20% bulk sampling confirmed that as bigger would be the bulk sampling fraction with respect to the tonnage of material, more precise and accurate would be the results. This is a handy method to get a real picture about our master alloys stock prior to manufacturing an alloy.

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