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Direct and indirect XRF methods of wear detection for binary and ternary alloy in organic media

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Abstract

Standard samples were prepared by employed fine powders of binary and ternary alloys were prepared and examined by XRF technique before immersed in organic liquid to determine the elemental composition. The powders suspended in organic liquids in different percentage and placed in special cell. The samples were subjected to x-ray beam. The same alloy were used as a plate and subjected to wear testing system. The wear rate was examine by two methods, weight loss method and XRF method. The absorption coefficient of elements were calculated mathematically and the results exhibited good agreement with real results.

Key words: XRF, Wear rate, binary alloy, Ternary alloy

1. Introduction

When the components of machinery move in contact with one another, natural wear process take place which results in the removal of wear material from surfaces [1-3]. The free material may be transported in the lubricant. Wear particles analysis are concerned with analyzing this material to determine the wear condition of the machine [4-6]. The rate of emission of wear particles from a particular source is the most direct indication of the extent of wear and for maintenance of the source. Thus, wear rates and debris (material lost by wear actions) composition are the measurable closest to the desired information on wear degree and wear sources [7, 8]. Most of the machine parts , suffer from friction and wear at the interfaces , this friction and wear affected the efficiency of machine and cause changes the mating parts .Wear particle analysis , seeks to determine the quantity of worn material ,the composition of the wear debris , and the wear rate of each source . X-ray fluorescence (XRF) involves radiating the samples with primary X-rays, which stimulate the sample to emit its own characteristic X-ray which then are analyzed [9- 16] X-ray are classified according to the technique used for determining spectral wave length or, equivalently, photon energy. The first technique called wavelength dispersive X-ray analysis (WDX) while the second called energy dispersive X-ray analysis EDX). In 1980 reports XRF for early damage detection in diesel motors and bearing. They were demonstrated the ability to use either dissolved metal or filtered metal particles to perform trending the engine wear. In 1980 Veiont [17-20] has published an important study of wear particulate analysis of samples taken from operational Helicopter engine. He compared between XRF method and c absorption method (AAS) for monitoring Fe and Cu by the measuring the dissolved material and suspended particulate in the liquid oil [21, 22].

2. Experimental procedure

2.1 Wear sample preparation

All samples were machined as a half bush .The important properties of the main materials used in the wear tests were shown in table 1. Each sample were first polished and cleaned using Acetone before wear test.

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Table 1: Important properties of the binary and ternary alloy used in this work.

Materials and supplier	Binary alloy (Brass), Westing house electronic company (USA Product)	Ternary alloy (Kovar) Westing house (USA Product)
Composition %	Cu:60, Zn:40	Fe: 53, Ni: 29, Co:18
Density	8.5 g/cm^3	8.36g/cm^3
Shape and dimensions	Half bush, D:1.6 cm, L:1.5	Half bush, D:1.6cm, L:1.5 cm

2.2 Wear test procedure

All wear samples were prepared and tested. Initial weight (for brass w_1=19.5026g and for kovar w_1=16.9827g) and final weights (W_1, W_2) for each sample were measured using sensitive balance of accuracy 10^{-4}g. Hardness was measured using hardness instrument type Brooks of U.K. product (hardness of brass = 39HRCand for kovar = 42HRC). Different sliding times were used (2 -10minutes) and the work done under different loads. The weight loss and hence the wear rate in each sample caused by wear process was determined after carefully cleaning the samples by acetone from oils All specimens were conducted to microscopic tests before and after each wear experiments for sliding time of 10 minutes using optical microscope type Rinkin of Japan product conducted with digital camera . The difference in weights (W) for each wear test was mainly dissolved in the oil for a fixed sliding speed (S.S =850rpm) .Two grams were taken from the oil under test for X-ray fluorescence analysis.

2.3 X-Ray fluorescence spectrometry (XRF)

A Siemens type SRS-200 sequential wavelength dispersive X-ray spectrometer was used to analyze all wear test samples under different conditions. The instrumental parameters are listed in table 2. A molybdenum (Mo) tube target was used to obtain high detection sensitivity for binary and ternary alloy.

Table 2: XRF conditions.

X-ray tube target	Mo
Power	30kv , 17mA
Atmosphere	10^{-6} bar
Specimen housing diameter	2.5cm
Analyzing crystal	LiF(100) with 2d 4.03^{o}A
Detection system	Scintillation counter

2.4 XRF-Direct method

The aim of this method is to determine qualitative and quantitative wear debris in oil for alloys half bushes .Two grams of oil under wear tests were taken for all wear samples and mixed with the organic solvent (2 ethanol-1hexanol)and placed in oil sample holder. X-ray fluorescence intensities were measured for all detectable elements. Intensity ratios (Kα –intensity divided by background intensity for each element) was found for each element and compared with the standard calibration curve Wear results by X-ray fluorescence technique will be compared with the weighing method for all samples.

2.5 XRF Indirect method for binary alloy

The aim of this method is to determine qualitative and quantitative wear debris in oil for unknown alloys. Two grams from oil under wear tests for binary alloy (Brass 60%Cu and 4o%Zn) were taken and placed in oil sample holder. XRF intensity measurements were conducted .Pure elements (Zn , Cu) were used as standard samples , and the Kα line intensities were measured for wear samples and for standard samples and by using the indirect method (calculation method) we can determine the elemental composition for samples under wear tests .

2.6 Sample calculations procedure

The calculations of this work obeys to the following remarks:

1. Determine the mass absorption coefficient of base oil experimentally as discussed.
2. Calculated the mass absorption coefficient of all samples by using software X-com programs [110].
3. Determine the alpha (α) factor according to the following) for all samples which were prepared.

$$\alpha_{ab} == \left[\frac{\mu_b(\lambda) + A\mu_b(a_{k\alpha})}{\mu_a(\lambda) + A\mu_a(a_{k\alpha})} - 1 \right] \quad (1)$$

Where $\mu_b(\lambda)$: mass absorption coefficient of element (a) at 2/3 from absorption edge of excited element (b).
A : Geometric factor as mentioned .
$\mu_b(a_{k\alpha})$: mass absorption coefficient of element (b) at ($a_{k\alpha}$)
$\mu_a(\lambda)$: mass absorption coefficient of element (a) at 2/3 from absorption edge of excited element (a) .
$\mu_a(a_{k\alpha})$: mass absorption coefficient of element a at ($a_{k\alpha}$) .

4. X-ray fluorescence measurements were conducted for all samples (standard and wear samples). All Kα line peak intensities were divided by background intensities as mentioned previously.
5. Calculate the relative intensity for all samples (intensity of element in alloy with in oil / intensity of the same pure element in oil).
6. Employing the following equations to determine the element compositions and confirm

That the wear debris of binary alloy founds in the base oil is related to Brass alloy, and then calculated the wear weight loss.

$$\alpha_{ab} = \frac{w_a}{w_b}(R_a - 1) \quad (2)$$

$$\alpha_{ba} = \frac{w_b}{w_a}(R_b - 1) \quad (3)$$

2.7 XRF Indirect method for ternary alloy

Two grams from organic(oil) under wear tests for ternary alloys (Kovar alloy) were taken and placed in sample holder . The line intensities for the elemental composition of Kovar ternary alloy were read in count per second. Nine specimens were prepared, three were pure metal elements Iron, Cobalt and Nickel with respect to which the intensity ratios were taken, six were all of the binary combinations of these elements mixed with 90% from oil for determine the empirical correction factors of the system. The line intensities were read in count per second for all samples for a given element. The composition of the prepared binaries are given in table 3. The X-ray intensity ratios (I.R = the intensity ratios of pure element / intensity of same element in alloy suspended in oil) of the binaries. The correction factor are calculated by employing the equations (2&3). The data of X-ray intensity ratios and correction factors are substituted into equations (4 A-C) to determine the simultaneous equations for Iron, Cobalt and Nickel. It is desirable to choose a calculating procedure which tends to minimize the errors.

$$(R_a - 1)w_a + \alpha_{ab}w_b + \alpha_{ac}w_c + \text{------} = 0 \quad \text{4 A}$$
$$\alpha_{ba}w_a - (R_b - 1)w_b + \alpha_{bc}w_c + \text{------} = 0 \quad \text{4 B}$$
$$\alpha_{ca}w_a + \alpha_{cb}w_b - (R_c - 1)w_c + \text{------} = 0 \quad \text{4 C}$$

Where R_a, R_a , R_a are the inverse of the relative intensities which where defined in equation (5). A solution of these equations can be obtained by adding another equation (7) as

$$R_i = f(w_a, w_b, w_c, \text{-----}) \quad (5)$$

Where R_i is the intensity ratio of element i $= I_i / (I_i)_p$ (6)
I_i is the relative intensity of element I, $(I_i)_p$ is the relative intensity of pure element i
w_a , w_b , w_c , -----, w_n are the fractional weight of elements a , b , c,------,

$$w_a + w_b + w_c = 1 \quad (7)$$

Table 3: The composition of the pure metals and the prepared binary alloys

No.	samples	W_{Fe} (%)	W_{Ni} (%)	W_{Co} (%)
1	Fe	100	-	-
2	Ni	-	100	-
3	Co	-	-	100
4	Fe-Ni	6.5	3.5	-
5	Fe-Co	7.5	-	2.5
6	Ni-Fe	4.0	6.0	-
7	Ni-Co	-	7.4	2.6
8	Co-Fe	3.2	-	6.8
9	Co-Ni	-	1.5	8.5

3. Results and Discussion

All fine powders were examined by XRF technique. The results shows that all these materials were pure. Standard solutions of Zinc, Copper, Nickel, Cobalt and Iron which were prepared by dissolving known weights of these pure powders in solution of 2ethanol-1hexanol were examined by X-ray fluorescence. A calibration curves for pure metals is prepared by plotting the ratio of Kα –intensity of metals to the background versus metal concentrations as illustrated in Figures 1- 4 for alloys (Brass and Kovar) in organic media (oil) .

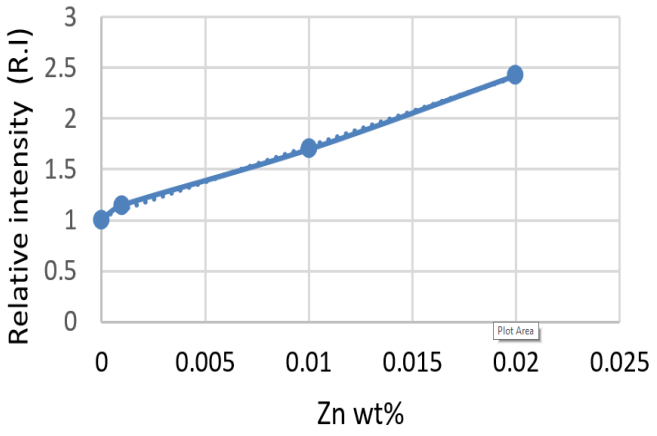

Figure 1 : Calibration curves for Zn suspended in oil

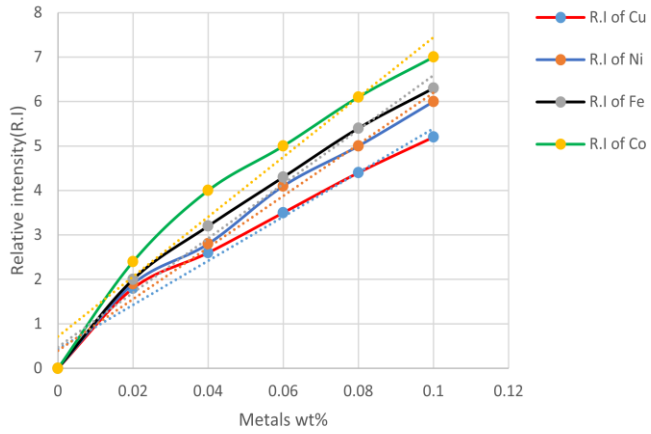

Figure 2: Calibration curves for pure metals in organic liquid

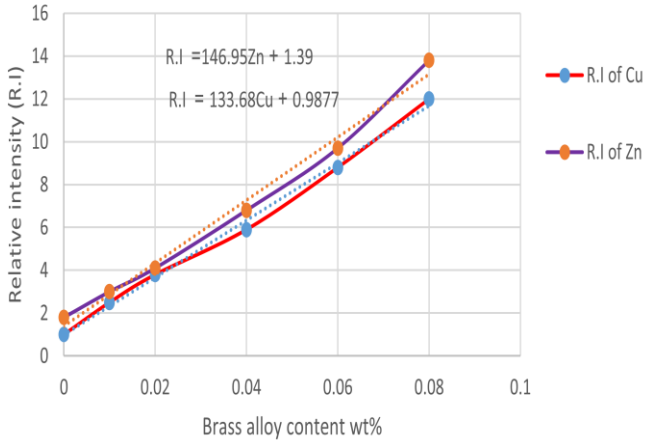

Figure 3: Calibration curves for brass alloys in organic liquid

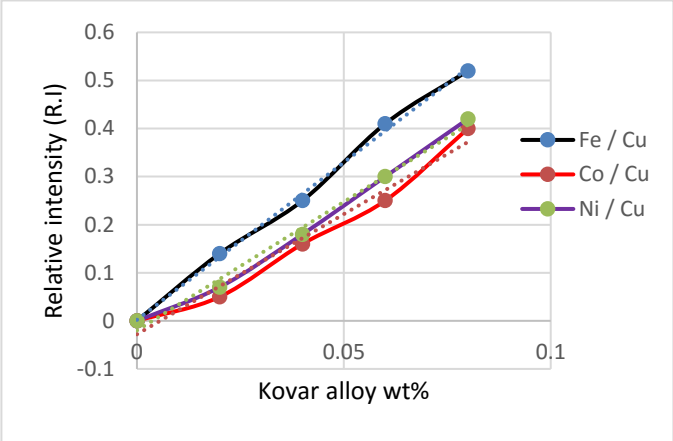

Figure 4: Calibration curves for Kovar alloys in organic liquid

3.1 Indirect method results

3.1.1 Binary metal alloy half bush results

Table 4 represents the mass absorption coefficient for base oil and Brass elements (Zn, Cu) at different wave lengths. The different wavelengths represents the excitation wave lengths for (Cu = 1.54°A, Zn = 1.435 °A) and 2/3 from the absorption edge (for Cu = 0.920, Zn = 0.855) [26]. As mentioned in the expression given in equation (2.12) , the α factor can be calculated from absorption coefficient, then the $\alpha_{Cu/Zn}$ = 0.1014and $\alpha_{Zn/Cu}$ = -0.0937. The Kα line intensities for pure elements (Zn, Cu) were measured and divided by background, then the intensity ratio of Zinc equal to 52.351 and of Copper equal to 46.37. The Kα line intensities for all binary metal alloys under wear tests at different wear conditions (normal loads and sliding time) are also divided by background .The relative intensity (R) (intensity ratio of wear samples / intensity ratio of standard samples (pure samples)) were calculated and tabulated in table 5 . By employing the equations (2.11Aand 2.12B)) are can determine the elemental concentrations of binary metal alloy (Brass) under wear tests in organic liquid . A sample calculation of indirect XRF-method for Brass elemental concentrations as will be as follows:

Table 4: The mass absorption coefficient at different wavelengths for standard samples.

μ(λ °A) samples	μ (0.855)	μ (0.92)	μ (1.435)	μ (1.54)
B.O	4.3230	4.652	7.2560	7.786
Cu	81.280	93.380	42.680	51.840
Zn	88.920	101.900	47.70	57.940

Table 5: XRF intensity ratio and the relative intensity(R) for binary metal alloy samples under wear tests at different wear conditions

Load (N)	Sliding time (min.)	Zn intensity ratio * (I.R)	Cu intensity ratio * (I.R)	R_{Zn} **	R_{Cu} **
	2	3.606	5.560	0.069	0.120
	4	4.741	7.069	0.090	0.152
	5	4.926	7.518	0.095	0.162
4	6	5.071	7.593	0.097	0.163
	8	5.203	8.058	0.100	0.172
	10	5.388	8.268	0.103	0.173
	2	3.843	5.749	0.073	0.124
	4	4.728	7.443	0.091	0.160
6	5	5.058	7.803	0.098	0.168
	6	5.388	8.268	0.103	0.178
	8	5.718	9.092	0.109	0.190
	10	5.823	9.197	0.114	0.196
	2	4.068	6.244	0.078	0.134
	4	5.718	8.673	0.110	0.186
9	5	5.850	9.312	0.113	0.200
	6	6.180	9.742	0.119	0.208
	8	6.681	10.570	0.130	0.226
	10	7.170	11.406	0.140	0.240

** Intensity ratio = Intensity of $I_{K\alpha}$ line peak / intensity of background*
*** Relative intensity (R) = intensity ratio of samples under wear tests /intensity ratio of standard (pure) element.*

Table 6 represents the comparison between XRF-indirect method (calculation method) results for brass elements concentrations and the actual concentrations (Zn=40%, Cu=60%). However the results reveals some deviations from actual composition may be due to some instrumental factors and to calculation method.

Table 6: Comparison between XRF- results for binary alloy concentrations

Loads (N)	Sliding time (min.)	Brass elements concentrations (wt%)	
		Zn	Cu
	2	36.45	63.55
	4	37.70	62.30
	5	37.00	63.00
4	6	37.31	62.69
	8	36.63	63.37
	10	37.32	62.68
	2	37.30	62.70
	4	36.10	63.90
	5	36.60	63.40
6	6	36.65	63.35
	8	36.67	63.33
	10	36.78	63.22
	2	36.80	63.20
	4	37.16	62.84
9	5	36.40	63.60
	6	36.52	63.48
	8	36.52	63.48
	10	36.84	63.16

3.1.2 Ternary metal alloy half bushes results

Table 7: represents the intensities of pure samples from Fe ,Co and Ni and the prepared binaries which were prepared at different concentrations with fixed base oil concentration (90wt%) . The correction factors were calculated (as will be shown in sample calculation) , and tabulated in Table 8 , The absorption factors are tabulated in table 9 , while table 10 represents the inverse of relative intensity (R) of Kovar ternary metal alloy samples under wear tests at different wear conditions (normal loads and sliding time) . The B.B algorithm was employed to calculated the elements concentrations in organic liquid samples of ternary alloy under wear tests

Table 7: XRF intensities ($I_{K\alpha}$) and the relative intensity of pure elements and standard binary alloys*

samples	$I_{K\alpha Fe}$ (c/s)	$I_{K\alpha Ni}$ (c/s)	$I_{K\alpha Co}$ (c/s)	R_{Fe}	R_{Ni}	R_{Co}
Fe-Ni	700	710	-	11.78	18.07	-
Fe-Co	770	-	480	10.71	-	21.77
Ni-Fe	490	1020	-	16.84	12.58	-
Ni-Co	-	1200	500	-	10.69	20.90
Co-Fe	420	-	930	19.64	-	11.12
Co-Ni	-	460	1120	-	27.89	9.33

Table 8: Absorbing parameters of Fe , Ni and Co

Absorbing elements	Radiating elements		
	Fe	Ni	Co
Fe	1.00	9.19	6.92
Ni	10.56	1.00	6.94
Co	8.77	4.74	1.00

Table 9: The relative intensities (R)of Kovar ternary metal alloy samples .

Load (N)	Sliding time (min.)	R_{Fe}	R_{Ni}	R_{Co}
4	2	9.37	49.38	55.00
	4	7.93	17.06	28.20
	5	7.37	17.01	27.00
	6	6.88	16.03	26.12
	8	6.76	15.84	23.75
	10	6.65	13.94	22.47
6	2	9.16	47.41	52.25
	4	7.20	16.40	26.12
	5	6.65	15.65	22.23
	6	6.60	13.53	20.49
	8	6.35	12.83	19.72
	10	6.28	11.66	19.18
8	2	8.78	44.24	47.50
	4	7.05	16.04	24.30
	5	6.57	15.10	20.50
	6	6.45	13.65	19.72
	8	6.30	12.58	19.35
	10	6.20	11.36	18.83

4. Conclusions

A calibration curves for pure metals is prepared by plotting the ratio of Kα –intensity of metals to the background versus metal concentrations gives good results for computed the the concentration of metal debris in organic liquids. The relative intensity (R) (intensity ratio of wear samples / intensity ratio of standard samples (pure samples)) can be used to determine the elemental concentrations of binary metal alloy under wear tests in organic liquid . Some deviations from actual composition may be due to some instrumental factors and to calculation method. The B.B algorithm represents active and accurate method when employed to calculated the elements concentrations in organic liquid samples of ternary alloy under wear tests

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