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Peertechz Journal of Medicinal Chemistry and Research
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CHEMISTRY GROUP

Open Journal of Chemistry

ISSN: 2641-3051 DOI: https://dx.doi.org/10.17352/ojc

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Received: 06 May, 2019
Accepted: 30 May, 2019
Published: 31 May, 2019

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Keywords: Aluminium alloys; Chromium; Diphenylcarbazide; Colorimeter; Absorbance; Concentration; Working curve

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Research Article

Colorimetric determination of chromium in aluminium alloys by diphenylcarbazide method

Abstract

A concise method for the determination of chromium in aluminium alloys colorimetrically by the use of diphenylcarbazide is described. The method is based on measurement of the violet colour formed between chromate III ion (Cr^{3+}) and diphenylcarbazide. The diphenylcarbazide forms a violet complex which absorbs at 540 nm. Other interfering metal ions including manganese and iron were masked by making alkaline with sodium hydroxide (NaOH). Potassium heptaoxodichromate (VI) $K_2Cr_2O_7$ solution (283ppm) was used as standard. Three aliquots (2ml, 5ml and 10ml) of standards were used for measurement. The solutions of samples were made in aquaregia and colour reagent added. Absorbance of standard as well as samples was measured at 540 nm using a colorimeter. A working curve obtained from known concentrations of standard was used to calculate the concentration of chromium in each sample. The findings show that colorimetric determination of chromium by diphenylcarbazide method is a simple, effective and valuable alternative method for the determination of chromium in aluminium alloys.

Introduction

The unique combinations of properties provided by aluminum and its alloys make aluminum one of the most versatile, economical, and attractive metallic materials for a broad range of uses. Aluminum alloys are economical in many applications. They are used in the automotive industry, aerospace industry, in construction of machines and in producing soft, highly ductile wrapping foils. They are also used in appliances and structures, as cooking utensils, as covers for housings for electronic equipment, as pressure vessels for cryogenic applications, engineering applications and in innumerable other areas [1]. Aluminum alloys are second only to steels in use as structural metals.

The mechanical, physical, and chemical properties of aluminum alloys depend upon composition and microstructure. The addition of selected elements to pure aluminum greatly enhances its properties and usefulness. Because of this, most applications for aluminum utilize alloys having one or more elemental additives. The major alloying additives used with aluminum are copper, manganese, silicon, magnesium, zinc and chromium. The total amount of these elements can constitute up to 10% of the alloy composition (all percentages given in weight percent). Impurity elements are also present, but their total percentage is usually less than 0.15% in aluminum alloys [1].

Chromium occurs as a minor impurity in commercial-purity aluminum (5 to 50 ppm). It has a large effect on electrical resistivity. Chromium is a common additive to many alloys of the aluminum-magnesium, aluminum-magnesium-silicon, and aluminum-magnesium-zinc groups, in which it is added in amounts generally not exceeding 0.35% [1]. In excess of these limits, it tends to form very coarse constituents with other impurities or additives such as manganese, iron, and titanium. This limit is decreased as the content of transition metals increases. In casting alloys, excess chromium will produce a sludge by peritectic precipitation on holding [1].

Many analytical techniques including spectroscopic [2], chromatographic [3], spectrophotometric [4] and absorption spectroscopy [5], have been described as useful for detection of chromium in Aluminium alloys. Some of these techniques are relatively costly and sophisticated and could be more time consuming hence, there is a need for a simpler analytical technique for the determination of chromium in Aluminium alloys.

Chromium has a slow diffusion rate and forms finely dispersed phases in wrought products. These dispersed phases inhibit nucleation and grain growth. Chromium is used to control grain structure, to prevent grain growth in aluminum-magnesium alloys, and to prevent recrystallization in aluminum-magnesium-silicon or aluminum-zinc alloys

Citation: Ayogu PC, Eze FI (2019) Colorimetric determination of chromium in aluminium alloys by diphenylcarbazide method. Open Journal of Chemistry 5(1): 009-012. DOI: http://dx.doi.org/10.17352/ojc.000011

during hot working or heat treatment [1]. The fibrous structures that develop reduce stress, corrosion susceptibility and/or improve toughness. Chromium in solid solution and as a finely dispersed phase increases the strength of alloys slightly. The main drawback of chromium in heat-treatable alloys is the increase in quench sensitivity when the hardening phase tends to precipitate on the pre-existing chromium-phase particles. Chromium imparts a yellow color to the anodic film [6].

The reasons why Aluminium and its alloys are in common use is because they have low density, they are easy to work with, they have high electrical conductivity, and they have high heat conductivity. However, aside from the advantages listed above, the engineering applications for Aluminium and alloys are limited due to poor surface properties, and low abrasion resistance [17]. For many commercial Aluminium alloys, the desirable mechanical properties are developed by adding alloys and applying heat treatment to heterogeneous microstructures. It is possible that adding alloying elements affects the wear properties of Al-Si-Mg, as it strengthens them through solid solution and hardening precipitation [7,8]. Ce, Cu, Cr, Fe, Mn, Ti, Zn, and Zr are some of the alloying elements that are added to these alloys. The added alloying elements either dissolve or form compounds within the microstructure. Over the years, a number of studies have been carried out to assess the effect specific intermetallic particles and individual alloying additives have on corrosion damage in Aluminium alloys, which arises from pitting and inter-granular type corrosion [9]. In situations where the corrosion characteristics of constituent intermetallics have been rigorously characterized, intermetallics have been found to exhibit a complex behaviour such as active and/or noble [10].

The intermetallics confirmed to exist within Aluminium alloys are: Mg_2Si, $MgZn_2$, $Al_{20}Cu_2Mn_3$, $Al_{12}Mn_3Si$, Al_7Cu_2Fe, Al_2Cu, Al_2CuMg, Al_3Fe, $Al_{12}Mg_2Cr$, $Al_{20}Cu_2Mn_3$, Al_6Mn, Al_3Ti, Al_3Zr, Mg_2Al_3, and $Al_{32}Zn_{49}$ [9,11,12]. The aim of this research is to qualitatively and quantitatively determine Chromium in Aluminium alloys using diphenylcarbazide method.

Materials and Methods

Collection of samples

The samples used for the analysis were locally sourced as follows;

Sample A - pebbles from a motorcycle hub were collected from Unwana Park, Ebonyi state, Nigeria. Sample B - drillings of aluminium window frames were gotten from Ariara Aba, Abia state, Nigeria. Sample C - pieces of aluminium roofing sheets were gotten from Ihe Nsukka, Enugu state, Nigeria. Sample D - base of an old television antenna was gotten from a waste bin in Calabar, Cross River State, Nigeria. Other reagents used for the analysis include; Diphenylcarbazide (Sigma Aldrich, U.S.A. ≥ 99 % purity), Potassium heptaoxodichromate (VI) $K_2Cr_2O_7$ (Sigma Aldrich, U.S.A. ≥ 99 % purity), Sodium hydroxide (Fluka, Sigma Aldrich, 99 % purity). Absorbance measurement were made with the Ciba Cornig Colorimeter (England) with 1cm cuvette.

Preparation of the solutions

Standard solution of potassium heptaoxodichromate (VI) was prepared by dissolving 0.283g of $K_2Cr_2O_7$ in 100ml of distilled water and diluting to $1dm^3$ in 1 L volumetric flask. Hence, the concentration of Chromium Cr (III) used is 283ppm.

Aqua regia was prepared by transferring 25ml HNO_3 using pipette into a reagent bottle followed by addition of 75ml HCL and 25ml of distilled water with the addition of concentrated tetraoxosulphate (VI) H_2SO_4 acid in small amount. The solution was made up to the required volume.

Qualitative analysis

Qualitative analysis were carried out for all the samples to determine the presence of chromium and aluminium in them using standard protocol as described by Ogburubi et al., [13]. Qualitative analysis were carried out for all the samples to determine the presence of chromium and aluminium as follows.

Test for aluminium

One drop of phenolphthalein and two drops of 2N CH_3COOH ethanoic acid were added to 2ml aluminium solution followed by 2 drops of $(NH4)_2CO_3$ ammonium trioxocarbonate (IV) (aluminium reagent). Formation of a red precipitate confirmed the presence of aluminium.

$$AL^{3+}{}_{(aq)} + 3(NH_4)_2\,CO_3 \rightarrow AL\,(CO_3)_3 + 6NH_4^-{}_{(aq)}$$

Test for chromium

One drop of phenolphthalein and two drops of ethanoic acid CH_3COOH were added to 2ml sample solution followed by one drop of 0.5 M $(CH_3COO)_2$ Pb lead ethanoate.

Formation of a yellow precipitate which dissolved on addition of 2ml 2N NaOH sodium hydroxide solution confirmed the presence of chromium.

Colorimetric determination

Suitable aliquots of the various sample solution were used for the analysis in accordance with the procedure for determination of chromium using the diphenyl carbazide method as follows (Ciba Cornig Colorimeter Instrument Mannual, 2010).

Each of the aluminium alloy (0.5g) sample A, B, C and D were successively dissolved in 15ml nitric acid, hydrochloric acid and distilled water in the ratio (1:3:1) and concentrated with 5ml tetraoxosulphate (VI) acid, H_2SO_4 solution. Each sample was evaporated to about 10ml by boiling till fumes of sulphur oxide were liberated. Distilled water (100 ml) was added and solution warmed to dissolve the sulphates. The solution was oxidized with two drops of nitric acid to remove the nitrous fumes and then diluted to 150 ml, cooled and 15 g ammonium per sulphate $(NH_4)_2S_2O_8$ added and boiled for 10 minutes. Then 1g of sodium chloride NaCl was added and solution boiled further to ensure complete reduction of manganese. This was cooled and 25 ml of 30% sodium hydroxide NaOH carefully added and was further boiled for another 10 minutes and cooled in running water and filtered. Filtrate was finally diluted to 200ml 20ml aliquot was pipetted into a 100 ml flask and 8ml of 25% tetraoxosulphate (VI) acid added. Aliquot was diluted to 80 ml followed by addition of 4 ml diphenyl carbazide solution and solution was made up to 100 ml. From the 100ml solution, the cuvette was filled with solution and introduced into sample port of the colorimeter. The colorimeter was set in the absorption mode and light allowed to pass through each sample solution at 540nm and the absorbance values was read up in the display. The instrument was initially set to zero with a blank solution and absorbance and concentration of standard measured. The data from the standard were used to establish a calibration curve from where concentration of each sample were obtained (Ciba Cornig Colorimeter Instrument Mannual, 2010) [14-17].

Results and Disscussion

Absorbance and concentration of chromium standards

The absorbance and concentrations of the various aliquots of chromium standards are given in table 1 and figure 1.

Absorbance and concentration of the samples

The absorbance and concentrations of the samples are given in table 2.

The result clearly revealed the actual amount of chromium present in each alloy of aluminium sample analysed. From the colorimetric determination, concentration values of 2900ppm, 2700ppm, 1000ppm and 700ppm were obtained for samples A, B, C and D respectively. The level or amount (ppm) of chromium was considered to give aluminium its unique properties of hardness, malleability and lustre, melting point as well as higher resistance to corrosion and discolouration.

Table 1: Absorbance and concentration (ppm) of chromium standards.

Aliquot	Absorbance (A)	Concentration (ppm)
2ml	0.03	400
5ml	0.14	2000
10ml	0.21	3000

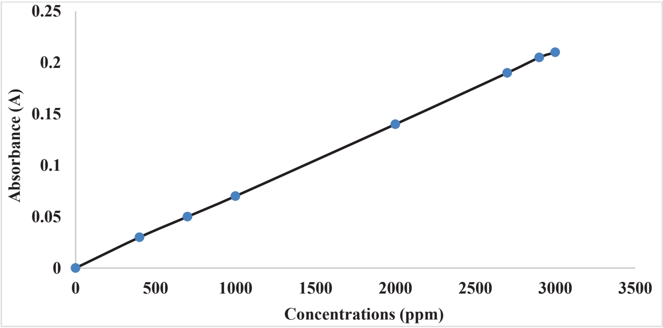

Figure 1: Working curve for the determination of Chromium concentrations of the samples.

Table 2: Absorbance and concentration (ppm) of the aluminium samples.

Samples	Absorbance (A)	Concentration (ppm)
A	0.21	2900
B	0.19	2700
C	0.07	1000
D	0.05	700

Conclusion

Previous reports show that, the presence of chromium helps to improve the qualities of aluminium products by enhancing their hardness, malleability, toughness, tempering and increasing their tensile strength and resistance to corrosion [9]. Due to the above properties, chromium has become a good alloying metal. The finding show that colorimetric determination of chromium by diphenylcarbazide method is a simpler, effective and valuable alternative method for the determination of chromium in aluminium alloys. In this study, it has been shown that many other metals could be used for alloying of the aluminium. Wrought aluminium alloy for example is made up of many alloying elements including silicon, iron, copper, zinc, magnesium, manganese, lead, etc. More researches are highly recommended to determine the presence as well as the amount of these other co-alloying metals in aluminium alloys. Also, the use of more rapid and sensitive procedures with possibly greater efficiency than the diphenyl carbazide method is recommended.

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Citation: Ayogu PC, Eze FI (2019) Colorimetric determination of chromium in aluminium alloys by diphenylcarbazide method. Open Journal of Chemistry 5(1): 009-012. DOI: http://dx.doi.org/10.17352/ojc.000011