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Chemical Analysis of Nickel-Manganese-Gallium Alloys

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Abstract

A method for the quantitative analysis of nickel-manganese-gallium alloys is presented. The method utilizes dissolution in nitric acid and quantitation by inductively coupled plasma – atomic emission spectroscopy. Memory effects due to adsorption of sample atoms onto instrument surfaces are also described.

Résumé

Le présent rapport contient la description d'une méthode de dosage pour les alliages nickel-manganèse-gallium. La méthode comprend une étape de dissolution dans l'acide nitrique et le dosage par spectroscopie d'émission atomique avec plasma induit par haute fréquence. L'adsorption de nickel, de manganèse et de gallium sur des surfaces mouillées de l'instrument entraîne des effets de mémoire et il faut donc, au besoin, effectuer des lavages à l'acide dilué entre chaque analyse d'étalon et d'échantillons.

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1. Introduction

The Ni_2MnGa alloy system has been identified as having a magnetic shape memory (MSM) effect [1]. Shape memory alloys have high actuation energies, energy densities and strains [2], making them potentially useful as actuator materials for a wide range of applications including flow control, sound transducers and sensors, vibration damping and micro-electro-mechanical systems (MEMS).

A martensitic crystallographic structure appears to be necessary to yield the MSM effect in Ni_2MnGa alloys [2]. The ability of the alloy to form martensitic structures is influenced by composition. For example, MSM effect has been demonstrated in $Ni_{48.5}Mn_{30.5}Ga_{21}$ and not in $Ni_{47.9}Mn_{33.3}Ga_{18.8}$ [3]. Therefore, control of alloy composition will be necessary for the development of Ni_2MnGa MSM actuator devices.

Despite the strong influence composition has on the existence of the desired MSM effect, most of the work on the Ni_2MnGa alloys systems has relied on energy dispersive x-ray spectrometry (EDXS) [4-7] and wavelength dispersive x-ray spectrometry (WDXS) [8] to determine composition. While these are useful non-destructive analysis techniques, their ability to quantitate to three significant figures is suspect. Typically, destructive chemical analysis techniques, such as inductively coupled plasma – atomic emission spectroscopy or atomic absorption spectroscopy, are required for this level of quantitation. Several instances of the use of these techniques to determine the composition of Ni_2MnGa alloys can be found in the literature [9-11], but details on the employed methodology were not provided.

Due to the lack of analysis detail, this paper describes a method for compositional analysis of Ni_2MnGa alloys utilizing inductively coupled plasma- atomic emission spectroscopy (ICP-AES).

2. Procedures and Results

Alloys for this work were prepared by Dr. Michael Gharghouri, Dalhousie University. Samples (~ 20 mg) were dissolved in approximately 20 mL of hot 50% nitric acid and then diluted to 100 mL.

Analyses were conducted using a Liberty II (Varian) ICP-AES. ICP instrument parameters utilized for the analyses are detailed in Table 1. These parameters were selected due to their success in the compositional analysis of other metal alloys, particularly steels.

Table 1. *ICP-AES Instrument Parameters*

PARAMETER	VALUE
Plasma gas rate	12 L/min
Auxiliary gas rate	0.75 L/min
PMT Voltage	650 V
Sample pump rate	15 rpm
Sample uptake delay	30 sec
Sample rinse time	10 sec

Emission lines for Ni, Mn, Ga and potential metallic contaminants were selected for sensitivity and lack of interferences from elements expected to be present in the alloy. Analysis parameters for each line are detailed in Table 2.

Table 2. *Element line parameters*

ELEMENT	WAVELENGTH (nm)	TRACKING WINDOW (nm)	RF POWER (KW)
Cobalt	228.616	0.027	1.50
Chromium	267.716	0.040	1.50
Copper	324.754	0.040	1.00
Iron	259.940	0.040	1.50
Gallium	294.364	0.040	1.00
Manganese	279.482	0.040	1.00
Nickel	231.604	0.040	1.50
Zinc	202.551	0.080	1.50

Quantitation was made against known elemental standards (Spex CertiPrep). For Ni, Mn and Ga, 100 mg/L standards were used while 10 mg/L standards were utilized for all other elements. 10% nitric acid was used as a blank. All elemental lines were analyzed using a 3 second interval and readings were taken in triplicate. Polynomial plotted background correction was employed for each line.

The results of ICP-AES analysis of three Ni_2MnGa alloys are shown in Table 3. The results shown are the average of 8 separate analysis of each alloy. Results are only shown for Ni, Mn and Ga content, as all other elements were present only at trace levels (< 0.1%).

Table 3: *Composition of Ni_2MnGa alloys*

ELEMENT	WEIGHT %		
	Alloy #1	***Alloy #2***	***Alloy #3***
Nickel	47.9	48.0	47.8
Manganese	21.1	21.9	22.3
Gallium	30.9	30.1	29.9

Table 4 shows statistical data for the analysis of Alloy #1, demonstrating the precision of the technique. Similar standard deviations and confidence intervals were obtained for the other alloys.

Table 4: *Confidence intervals (CI) for analysis technique.*

ELEMENT	AVERAGE	STD DEV	95% CI
Nickel	47.9	0.9	± 0.6
Manganese	21.1	0.6	± 0.4
Gallium	30.9	0.4	± 0.3

It is possible for sample atoms to interact with surfaces within the instrument. Some elements adsorb onto these surfaces and then release during subsequent sample introduction. This is usually termed as a “memory effect” and can lead to erroneous sample and blank readings. This effect was observed with these alloys.

This is demonstrated in Figure 1. A 10% nitric acid blank was introduced into the ICP and analyzed for Mn content, as described above. This is shown as the green trace in

Figure 1. Following this, a 100 mg/L sample of Mn was introduced. Note that this run is not shown on the Figure. Afterwards, the same 10% nitric acid blank was re-run three additional times. These runs are shown as the blue, brown and magenta traces in the Figure. This demonstrates that Mn from the 100 mg/L standard adsorbed onto instrument surfaces and was released during subsequent runs. Similar memory effects can be demonstrated for Ni and Ga.

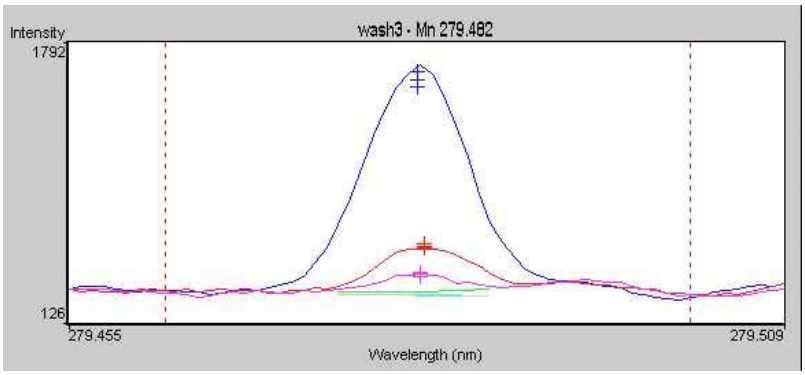

Figure 1: Memory effect for manganese. Green trace is initial 10% nitric acid blank. Blue, brown and magenta traces are sequential runs of same blank after run (not shown) of 100 mg/L Mn. These traces show false levels of Mn resulting from instrument memory effect.

The memory effect shown here has only a minor affect on analysis results, typically on the order of 0.1 to 0.2 weight percent. Its affect can be minimized by running a 10% nitric acid wash between each standard and sample.

The Varian Liberty ICP-AES utilizes a photo-multiplier tube (PMT) to detect photonic radiation emitted as excited analyte atoms in the plasma return to the ground state. The number of photons thus detected is called the "intensity" and is used to quantitate the amount of a particular element present in a sample by comparison to intensities recorded for known elemental standards. For an analysis to be quantitative, the intensity of both the standards and analytes must remain consistent.

Solutions of dissolved metallic elements, whether they are standards or analytes, can degrade over time, generally due to precipitation of the elements. For any analysis technique, it is therefore important to determine the length of time over which standards and analytes can be expected to remain stable. This was done for the 100 mg/L elemental standards and dissolved NiMnGa alloys used in this report by measuring and plotting PMT intensities over a 10 day period. These plots are shown in Figures 2 and 3.

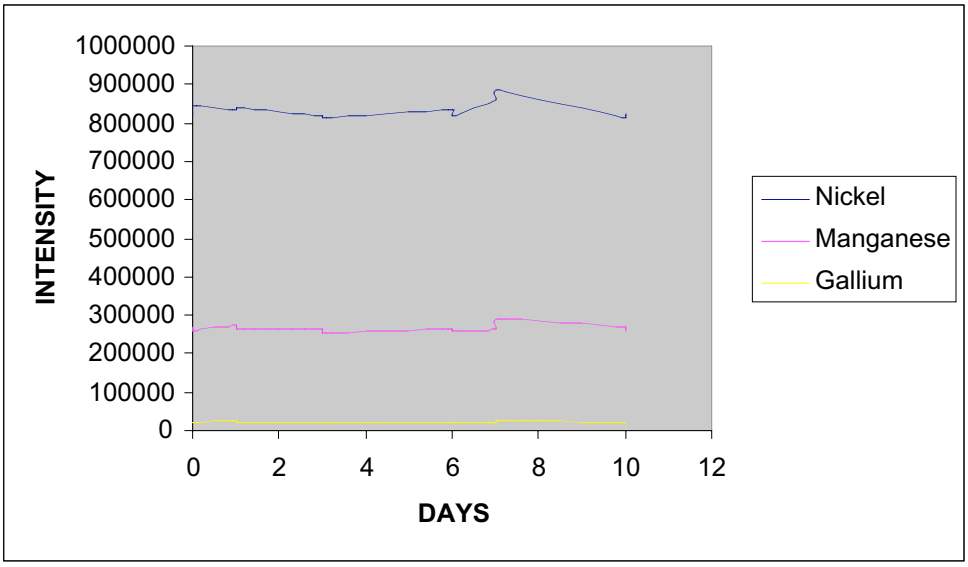

Figure 2: Plots of intensities recorded for 100 mg/L standards of Ni, Mn and Ga over a 10 day period.

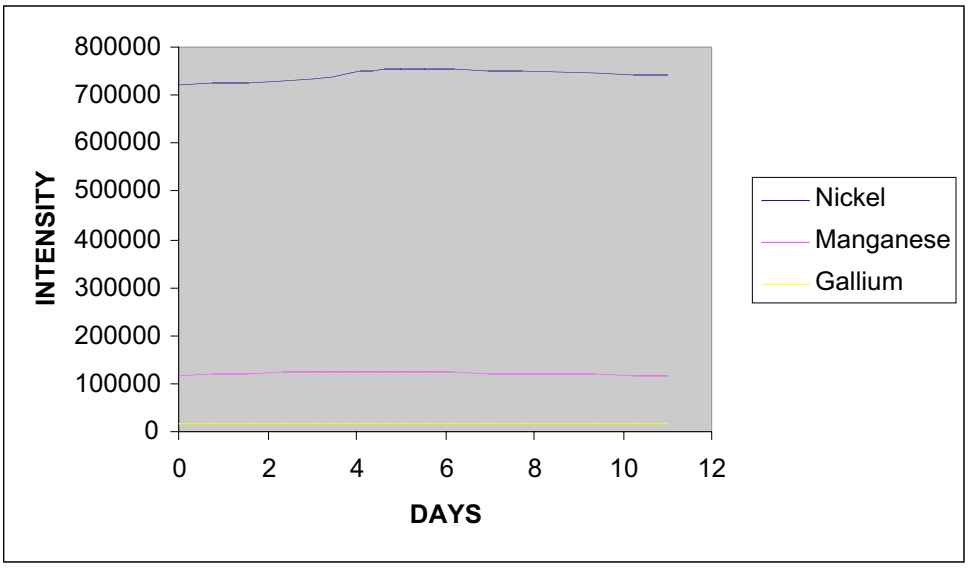

Figure 3: Plots of intensities of Ni, Mn and Ga in NiMnGa alloy #1 recorded over a 10 day period.

These plots indicate that the standard and dissolved alloy solutions are stable for at least 10 days.

3. Conclusions

An accurate and precise technique for the quantitative analysis of Ni_2MnGa alloys has been demonstrated. The method employs nitric acid dissolution of the alloy followed by quantitation of alloying elements by inductively coupled plasma – atomic emission spectroscopy.

It was discovered that nickel, manganese and gallium, adsorbed onto wetted surfaces in the ICP. These adsorbed materials were leached out during subsequent standard or sample introduction adversely affecting results. The use of dilute nitric acid washes between individual standards and samples corrected this problem.

Elemental standards and dissolved NiMnGa alloys were found to be stable for at least 10 days.

Future work in this area will include a rigorous comparison of the capabilities of EDXS versus ICP-AES for the analysis of NiMnGa alloys.

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List of symbols/abbreviations/acronyms/initialisms

CI	Confidence interval
EDXS	Energy dispersive x-ray spectrometry
ICP	Inductively coupled plasma
ICP-AES	Inductively coupled plasma – atomic emission spectrometry
KW	Kilowatt
L/min	Litres per minute
MEMS	Micro-electro-mechanical systems
mg	Milligrams
mg/L	Milligrams per litre
mL	Millilitres
MSM	Magnetic shape memory
nm	Nanometres
PMT	Photomultiplier tube
RF	Radiofrequency
rpm	Revolutions per minute
sec	Second
Std dev	Standard deviation
V	Volt
WDXS	Wavelength dispersive x-ray spectrometry

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