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Chemical Characterisation of Bulk and Melt-spun Ribbons of *NiMnIn* Alloy using Inductively Coupled Plasma Optical Emission Spectrometry

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ABSTRACT

Method development for the analysis of *NiMnIn*, a new magnetocaloric effect (MCE) material using inductively-coupled plasma optical emission spectrometry (ICPOES) is discussed. Spectral interference of *Ni* and *Mn* on the analysis of *In* were studied. The process of method validation was carried out using various analytical techniques like conventional wet chemical techniques and instrumental techniques such as atomic absorption spectrometry. All the techniques show a close agreement in values, thus this method could be applied for regular analysis of *NiMnIn* alloys. A comparative chemical analysis of bulk and melt-spun ribbons of this alloy is also discussed.

Keywords: Chemical analysis, *Nickel-Manganese-Indium* alloy, ICPOES, method development, magnetocaloric effect material

1. INTRODUCTION

Success of any material development programme depends on the analytical data obtained by various analytical techniques. Chemical characterisation is the first and foremost characterisation technique carried out while developing new materials, as the properties of a material largely depend on its chemical composition. Hence, quality of analytical data obtained plays a crucial role in the development of new alloy systems. The procedures adopted for method development and the means followed for its validation directly impact the quality of analytical data. A common, problem that frequently arises during chemical analysis is interference; it could be either chemical or spectral in origin, either of which leads to wrong chemical values. The best way to minimise this problem is through proper validation of analytical method using suitable certified reference materials (CRMs). This is important wrt quality assurance and quality control of chemical measurements.

The exotic properties like ferro-magnetic shape memory[1, 2] (FMSM) and giant magneto caloric effect[3-5] (GMCE) exhibited by *Nickel-Manganese-Indium (NiMnIn)* alloy system makes it an interesting functional material. The FMSM effect arises from the magnetostrictive deflections through twin boundary movement and only specific compositions of *NiMnIn* alloys exhibit this property. These alloy systems have a unique combination of high strains, high actuation frequency (over 5kHz has been measured) and large energy densities, which make them potential materials for a variety of military and civilian applications. Envisaged defence applications include devices for vibration and signature control, energy harvesting, aerodynamic and hydrodynamic control systems, active shock amelioration systems, sonar devices and microactuators[6,7] in nose cones of propelled projectiles.

GMCE is generally exploited for civilian applications such as magnetic refrigeration. This system is pursued widely due to its ease of processing, eco-friendliness and cost-effectiveness. One important aspect from application point of view is that all magnetic refrigeration materials should have magnetic transformation (T_C) and structural transformation (T_M) temperatures to be very close to the room temperature[8]. A change of even 1per cent in composition of the alloy shifts the structural transformation temperature[9-11], by at least 30 °C. Owing to the large variation in behaviour with slight change in composition, it becomes very crucial to know the precise final composition of the alloy after preparation.

The present study discusses the chemical analysis of bulk and melt-spun ribbons of *NiMnIn* using inductively coupled plasma optical emission spectrometry (ICPOES) and possible spectral interferences in the analysis. The method validation process using various other analytical techniques such as conventional (gravimetry, volumetry) and instrumental (Atomic Absorption Spectrometry -AAS) has been described in detail. Method validation using three different techniques is necessitated by the fact that each technique has its own drawbacks, such as spectral interferences in the case of optical emission spectroscopy[12-14] and chemical interferences in the case of conventional and absorption spectroscopy[15]. This exercise is very important, as it is a new material under development, which has neither CRMs nor standard operating procedures.

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2. EXPERIMENTAL

2.1 Materials and Reagents

All the mineral acids used were supra pure grade purchased from Aldrich. Single elemental standards for ICPOES were purchased from Merck Labs. High purity water with a resistivity of 18.2 MΩcm obtained from Euro 10 purifier (M/s. SG, Germany) was used for all the experiments.

2.2 Dissolution of Samples

Approximately 0.1 g of the powder in case of bulk sample and 0.1 g of ribbon pieces in case of ribbon samples were weighed on an analytical balance and transferred into an express microwave digestion vessel and to it 8 ml of aquaregia ($HCl + HNO_3$ in 3:1 ratio, respectively) was added. The vessel was kept in a microwave accelerated reaction system (MARS) (M/s. CEM Corporation) for digestion. The program was made so as to hold the sample at a temperature of 80 °C for 15 min. The system was allowed to cool down for 15 min and then the dissolved sample was transferred into a 100 ml volumetric flask and made up to the mark with water. From this stock solution, 10 ml aliquot was pipetted out and diluted ten times before analysis.

2.3 Procedures

As CRMs were not available for carrying out the validation process of analysis for this particular alloy system, single element ICP standards were used for the preparation of three synthetic standard solutions, with varying concentrations of *Ni*, *Mn*, and *In*, keeping in mind the typical compositions used for obtaining the GMCE. The compositions used as synthetics are presented in Table 1.

Table 1. Concentrations of various synthetic standards prepared

Code	*Ni* (ppm)	*Mn* (ppm)	*In* (ppm)
Synthetic 1	40	20	15
Synthetic 2	50	30	25
Synthetic 3	60	40	35

These synthetic standards were further used as samples for analysis in ICPOES. For the calibration of method, single element standards of each element with necessary dilutions were prepared from a 1000 ppm stock solution. An acid blank with 8 ml aqua regia in 100 ml water was used as zero concentration solution. For the construction of calibration graphs for each element, the following concentrations were used:

- *Ni*: 0, 20, 40, 60, 80, and 100 ppm;
- *Mn*: 0, 10, 20, 30, 40, and 50 ppm;
- *In*: 0, 10, 20, 30, 40, and 50 ppm.

In ICPOES, initially three spectral lines for each element were chosen based on their limits of detection and observed for any possible interferences from the other two constituent elements on the analyte. The lines chosen for each element were:

- *Ni*–216.556 nm, 231.604 nm, and 352.454 nm;
- *Mn*– 257.610 nm, 259.373 nm, and 260.569 nm; and
- *In*–230.606 nm, 303.936 nm and 451.130 nm.

The ICPOES instrument used for analysis is a sequential JY Ultima model (M/s. Jobin Yvon, France). The spectrometer includes a 40.68 MHz free running oscillator for driving the radially viewed plasma, an echelle grating for wavelength separation and a grid nebuliser for sample aspiration. Various operating parameters are given in Table 2.

Table 2. Plasma operating conditions for ICPOES

Parameter	
Power	1.0 kW
Plasma gas	14 l/min
Nebulizer pressure	280 kPa
Auxiliary gas	1.5 l/min
Sample introduction	1 ml/min
Integration time	12 s

For method validation, the same synthetic standards were analysed using wet chemical methods and AAS, the instrument used in the present work is Avanta model (GBC, USA); the parameters used for analysis are hollow cathode lamps as primary source of irradiation with lamp current of 5 mA and slit width of 0.2 nm. An air/ acetylene flame was used for excitation of the atoms. The wavelengths chosen for analysis of each element in AAS are listed:

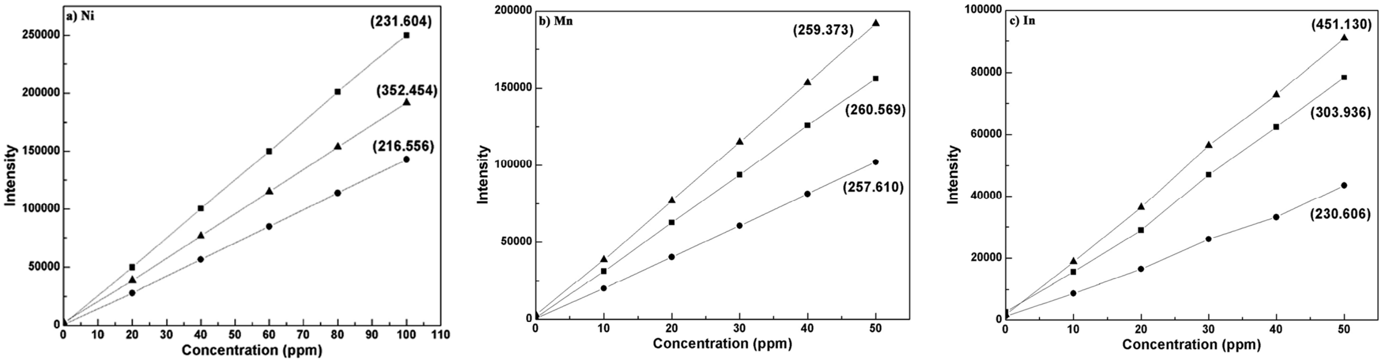
- for *Ni*- 341.5 nm, 351.5 nm, and 352.4 nm,
- for *Mn*- 279.8 nm, 280.1 nm, and 403.1 nm, and
- for *In*- 271.0 nm, 303.9 nm, and 325.6 nm.

In conventional route nickel was analysed by gravimetry using DMG method[16], whereas *Mn* was analysed using EDTA titration[17] and *In* was analysed by gravimetric route by first precipitating it as sulphide using H_2S[18].

3. RESULTS AND DISCUSSION

Figure 1 shows the calibration plots obtained from ICPOES for each analyte: a) *Ni*, (b) *Mn*, and (c) *In*, at all three selected wavelengths. From Fig. 1 it is evident that all the lines show a linear behaviour in the concentration range of interest. In case of indium, analysis of the three lines chosen, at 230.606 nm a wing overlap from *Ni* 230.640 nm and at *In* 303.936 nm a similar overlap from *Mn* 303.955 nm was observed. The other line 451.130 nm was devoid of any such interference and therefore chosen for carrying out further studies. Whereas for *Ni* and *Mn* no such spectral interferences were observed from the matrix elements at all the selected wavelengths, so background equivalent concentrations (BEC) for the remaining two elements were measured at the respective wavelengths of the analyte. Based on the lowest BEC values, the following lines for each element were chosen for creating a sequential analysis program, *Ni*- 231.604 nm, *Mn*- 257.610 nm, and *In*- 451.130 nm.

Similarly, based on the linear behaviour in the concentration range mentioned and on the basis of lower BEC values, the following lines were preferred over the others for analysis in AAS and these are as follows, *Ni*-351.5 nm, *Mn*-403.1



(a) (b) (c)

Figure 1. Calibration graphs obtained from ICPOES at different wavelengths for (a) *Ni*, (b) *Mn*, and (c) *In*.

nm, and *In*-303.9 nm.

After method calibration, the synthetic standards were aspirated as samples and their concentrations were obtained which are tabulated along with the values obtained from conventional routes in Table 3. All the values reported are an average of five readings and their standard deviations are mentioned in parenthesis. Values obtained are all having a relative standard deviation of less than 2 per cent. From the values tabulated in Table 3, it is evident that all the values obtained using from three different techniques are in fair agreement with each other, and hence, the method is applicable for analysis of actual samples.

The analytical results obtained on analysis of six actual samples code named B1-3 for bulk and R1-3 for ribbons made using melt spinning are furnished in Table 4. From Table 4, it is clear that the values obtained by three different techniques for the same sample are in good agreement, which infers that there is no interference of

Table 3. Analytical results obtained for synthetic mixtures (in ppm)

Element	Technique	Synthetic 1	Synthetic 2	Synthetic 3
Ni	ICPOES	40.1 (0.3)	50.2 (0.2)	60.0 (0.1)
	AAS	40.0 (0.1)	50.1 (0.2)	59.8 (0.4)
	Conventional	40.2 (0.2)	49.8 (0.3)	60.1 (0.3)
Mn	ICPOES	19.9 (0.1)	30.1 (0.2)	40.3 (0.2)
	AAS	19.8 (0.2)	29.8 (0.3)	39.9 (0.2)
	Conventional	20.0 (0.2)	29.9 (0.2)	40.2 (0.2)
In	ICPOES	15.1 (0.1)	25.2 (0.2)	35.1 (0.3)
	AAS	14.9 (0.2)	24.8 (0.1)	35.2 (0.2)
	Conventional	14.7 (0.2)	25.2 (0.3)	34.9 (0.3)

Table 4. Comparative evaluation of analytical results obtained for real samples

Code	Analytical Method	Composition (Wt%)		
		Ni	*Mn*	*In*
B1	ICPOES	44.8 (0.3)	33.6 (0.2)	21.6 (0.1)
	AAS	44.7 (0.4)	33.6 (0.1)	21.7 (0.2)
	Conventional	45.0 (0.3)	33.8 (0.2)	21.7 (0.2)
B2	ICPOES	42.6 (0.3)	35.5 (0.2)	21.9 (0.1)
	AAS	42.5 (0.3)	35.7 (0.1)	21.6 (0.1)
	Conventional	42.8 (0.3)	35.8 (0.2)	21.7 (0.2)
B3	ICPOES	41.1 (0.3)	37.1 (0.1)	21.8 (0.2)
	AAS	41.0 (0.1)	37.3 (0.1)	21.9 (0.1)
	Conventional	41.3 (0.4)	37.0 (0.2)	21.6 (0.2)
R1	ICPOES	44.6 (0.3)	33.2 (0.1)	22.2 (0.1)
	AAS	44.8 (0.2)	33.1 (0.1)	22.3 (0.2)
	Conventional	44.9 (0.3)	33.3 (0.1)	22.1 (0.1)
R2	ICPOES	42.5 (0.1)	35.0 (0.2)	22.4 (0.1)
	AAS	42.3 (0.4)	35.1 (0.1)	22.3 (0.2)
	Conventional	42.6 (0.2)	35.3 (0.2)	22.3 (0.1)
R3	ICPOES	41.2 (0.3)	36.5 (0.1)	22.4 (0.2)
	AAS	41.3 (0.2)	36.4 (0.2)	22.2 (0.1)
	Conventional	41.4 (0.3)	36.6 (0.2)	22.3 (0.2)

one element on the other at the specified lines. As the ribbons were prepared from the same bulk samples, comparison of the bulk to ribbons showed an interesting behaviour. The values of *Ni* remained more or less the same in case of both bulk and ribbons, but in case of *In* a slight increase to the tune of 0.5 wt % was observed in all the ribbons when compared to their bulk counterparts and to the same tune there was a decrease observed in *Mn* values for all the ribbons. From the data data it could be inferred that during the processing of ribbons, the desired composition of bulk is not being retained and this small variation could have a large effect on the final properties of the material.

4. CONCLUSIONS

From this study it can be concluded that the sequential multi-elemental method described for analysis of these alloys using ICPOES is very precise as the possibility of interferences were ruled out by proper method validation procedure including the comparative evaluation of values with other techniques. The method described not only provides accurate analysis but also helps in increasing the time efficiency. Also a comparative evaluation between bulk and ribbons provides a better insight for optimising the processing parameters for ribbons.

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REFERENCES

1. Krenke, T.; Acet, M. & Wassermann, E.F. Ferromagnetism in the austenitic and martensitic states of *Ni-Mn-In* alloys. *Physics Review B*., 2006. **73**(17), 174413, 1-10.
2. Han, Z.D.; Wang, D.H.; Zhang, C.L.; Xuan, H.C.; Zhang, J.R.; Gu, B.X. & Du, Y.W. The martensitic transformation and the magnetocaloric effect in $Ni_{50-x}Mn_{38+x}In_{12}$ alloys. *Solid State Commun.,* 2008, **146**(3-4), 124-27.
3. Zhang, X.; Zhang, B.; Yu, S.; Liu, Z.; Xu, W.; Liu, G.; Chen, J.; Cao, Z. & Wu, G. Combined giant inverse and normal magnetocaloric effect for room-temperature magnetic cooling. *Physics Review B,* 2007. **76**(13), 132403 (1-4).
4. Miyamoto, T.; Ito, W.; Umetsu, R.Y.; Kainuma, R.; Kanomata, T. & Ishida, K. Phase stability and magnetic properties of $Ni_{50}Mn_{50-x}In_x$ Heusler-type alloys. *Scripta Materialia* 2010, **62**(3), 151-54.
5. Zhao, X.G.; Hsieh, C.C.; Lai, J.H.; Cheng, X.J.; Chang, W.C.; Cui, W.B.; Liu, W. & Zhang, Z.D. Effects of annealing on the magnetic entropy change and exchange bias behaviour in melt-spun *Ni-Mn-In* ribbons. *Scripta Materialia,* 2010, **63**(2), 250-53.
6. Hernando, B.; Sánchez, J.L.; Santos, J.D.; Sánchez, M.L.; Escoda, L.; Suñol, J.J.; Varga, R.; García, C. & Gonzalez, J. Grain-oriented *NiMnSn* and *NiMnIn* Heusler alloys ribbons produced by melt-spinning: Martensitic transformation and magnetic properties. *J. Magntsm. Magn. Mater*., 2009, **321**(7), 763-68.
7. Aliev, A.M.; Batdalov, A.B.; Kamilov, I.K.; Koledov, V.V.; Shavrov, V.G.; Buchelnikov, V.D.; García, J.; Prida, V.M. & Hernando, B. Magnetocaloric effect in ribbon samples of Heusler alloys *Ni-Mn-M* (*M=In*,*Sn*). *Appl. Phys. Lett.,* 2010, **97**(21), 212505 (1-3).
8. Han, Z.D.; Wang, D.H.; Zhang, C.L.; Tang, S.L.; Gu, B.X. & Du, W.Y. Large magnetic entropy changes in the $Ni_{45.4}Mn_{41.5}In_{13.1}$ ferromagnetic shape memory alloy. *Appl. Phys. Lett*., 2006. **89**(18), 182507 (1-3).
9. Pathak, A.K.; Khan, M.; Dubenko, I.; Stadler, S. & Ali, N. Large magnetic entropy change in $Ni_{50}Mn_{50''x}In_x$ Heusler alloys. *Appl. Phys. Lett.,* 2007, **90**(26), 262504 (1-3).
10. Chattopadhyay, M. K.; Manekar, M. A.; Sharma, V. K.; Arora, P.; Tiwari, P.; Tiwari, M. K. & Roy, S. B. Contrasting magnetic behaviour of $Ni_{50}Mn_{35}In_{15}$ and $Ni_{50}Mn_{34.5}In_{15.5}$ alloys. *J. Appl. Phys.,* 2010, **108**(7), 073909 (1-10).
11. Rao, N.V.R.; Chandrasekaran, V. & Suresh, K.G. Effect of *Ni*/*Mn* ratio on phase transformation and magnetic properties in *Ni–Mn–In* alloys. *J. Appl. Phys.*, 2010, **108**(4), 043913 (1-7).
12. Bings, N.H.; Bogaerts, A. & Broekaert, J.A.C. Atomic spectroscopy. *Analytical Chemistry*, 2008, **80**(12), 4317–4347.
13. Kavipurapu, C.S.; Gupta, K.K.; Dasgupta, P.; Chatterjee, N.N. & Pandey, L.P. Determination of boron in steels by inductively-coupled plasma optical emission spectrometry. *Analysis*, 1993, **21**(1), 21-24.
14. Nakahara, T. Determination of phosphorous in steels and copper metals by vacuum ultraviolet atomic emission spectrometry with inductively-coupled plasma. *Spectrochimica Acta B: Atomic Spectroscopy*, 1985, **40**(1-2), 293-300.
15. Kula, I.; Arslan, Y.; Bakiredere, S.; Titretir, S.; Kendüzler, E. & Ataman, O.Y. Determination and interference studies of bismuth by tungsten trap hydride generator atomic absorption spectrometry. *Talanta,* 2009, **80**(1), 127-32.
16. Vogel, A. *In* A textbook on quantitative inorganic analysis including elementary instrumental analysis. 1962. pp. 434-80.
17. Ueno, K.; Imamura, T. & Cheng, K.L. *In* Handbook of organic analytical reagents. 1992. pp. 213-14.
18. Hopkins, C. Analysis of indium alloys. *Ind. Eng. Chem. Anal.* 1942, **14** (8), 638-39.

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