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SYNTHESIS OF NICKEL BASE ALLOYS FOR USE AS MAGNETIC STANDARDS

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Abstract

The goal of this research is to prepare a series of alloys having sharp, reproducible magnetic transitions for calibrating temperature in thermogravimetry from the magnetic transition temperature of pure cobalt (1121°C) to below room temperature.

Alloys in the Ni–Co and Ni–Cu systems were prepared by the thermal decomposition of co-precipitated oxalates in argon. The alloys were subsequently annealed under 5% hydrogen.

Magnetic transition temperatures were measured using simultaneous thermomagnetometry/differential thermal analysis. Transition temperatures were corrected using well known meltingpoint standards. Magnetic transition temperatures along with precision are reported as a function of composition.

Keywords: magnetic standards, thermomagnetometry

Introduction

Norem *et al.* [1] first proposed the use of magnetic materials as temperature standards for TG instruments. By placing a small, permanent magnet above or below the sample, an apparent weight gain or loss is observed as the material reaches the temperature, T_c, where it undergoes a ferro or ferrimagnetic to paramagnetic transition. These materials offer the advantages of calibrating temperature directly at the sample position and running several standards simultaneously.

The widespread acceptance of this method led to a detailed study [2] of the magnetic transition temperatures of nickel and four magnetic alloys, resulting in their availability as TG temperature standards through N.I.S.T. (National Institute of Standards and Technology). Individual participants in this study showed good precision in their measurements, but results between laboratories varied widely, leading to high standard deviations in the reported mean T_c values.

Gallagher *et al.* [3] and Weddle *et al.* [4] demonstrated that these large deviations were due in part to the temperature calibrations of the various instruments used in the study Using simultaneous TG/DTA techniques, melting point standards can be run together with a magnetic standard. T_c can then be corrected using melting points which define the International Temperature Scale of 1990 [5] by simply choosing melting point standards whose melting points surround T_c.

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Even using this technique, however, the transition temperatures of a number of the currently used alloys have sizable standard deviations [4]. Various compositions of Ni–Co and Ni–Cu alloys have, therefore, been prepared as possible substitutes for the currently available series of magnetic temperature standards. By varying the Ni:Co ratio, transition temperatures throughout the entire range between the magnetic transition of pure cobalt and that of pure nickel can be achieved [6, 7]. Likewise, by varying the Ni:Cu ratio transition temperatures throughout the range below the magnetic transition temperature of pure nickel can be achieved.

Experimental procedures and results

Ni–Co and Ni–Cu alloys were prepared by the thermal decomposition of coprecipitated nickel–cobalt and nickel–copper oxalate dihydrates [8]. Coprecipates were formed using the 'clean oxalate' technique [9, 10]. Nickel and cobalt or copper carbonates were mixed in the desired proportions into an aqueous slurry. This slurry was added to a three percent excess of aqueous oxalic acid solution, heated to 75°C, and stirred overnight. The resulting coprecipitates were filtered, washed several times with water, and rinsed finally with acetone. Once dry, the coprecipitates were ground to a fine powder in a mortar and pestle.

The coprecipitates were decomposed to form the alloys by heating to 500°C for several hours in a tube furnace under flowing argon. The alloys were then annealed at 1000°C under flowing 5% hydrogen/95% nitrogen for several days to ensure full reduction and homogeneity of the samples and to remove residual carbon left from the decomposition of the coprecipitates.

Magnetic transition temperatures were measured using a Seiko Model 320 simultaneous TG/DTA with a horizontal balance configuration. A small, permanent magnet placed on top the furnace provided the necessary magnetic gradient. Melting point standards were chosen which bracketed or nearly bracketed the magnetic transition of the alloy. The melting point standard with the lowest heat of fusion was placed in the sample pan first, then covered with a thin layer of alumina powder. The second melting point standard was placed on the alumina layer and was covered by yet another layer of alumina powder. Finally, the alloy was placed on top. The instrument was purged with 5% hydrogen/95% nitrogen (200 ml min^{-1}) for 1/2 h before starting any run. The heating rate used was 10°C min^{-1}.

Magnetic transition temperatures were corrected using the slope of an observed temperature *vs.* actual temperature plot constructed from the melting point data. The results are summarized in Table 1.

Discussion

Multiple measurements of transition temperatures for the Ni–Co and Ni–Cu series of alloys were fairly consistent, making them reasonable alternatives to the currently accepted series of magnetic standards. The magnetic transitions of both series of alloys appeared sharp, and duplicate samples in the Ni–Co series showed nearly the same transition temperatures, suggesting homogeneity of the samples.

Surprisingly, the corrected transition temperatures have higher standard deviations than the uncorrected transition temperatures. This is contrary to previously

Table 1 Measured values of melting temperatures of melting point standards and measured and corrected values of T_c of various magnetic alloys

T_m^{obs}	T_m^{obs}	T_c^{obs}	T_c^{obs}avg	$T_c^{obs}\sigma$	T_c^{corr}	T_c^{corr}avg	$T_c^{corr}\sigma$
Ag	Au	$Ni_{0.33}Co_{0.67}$					
*	*	1000.3					
*	*	998.8					
*	*	996.6					
*	*	996.0	997.9	1.9889			
Ag	Au	$Ni_{0.33}Co_{0.67}$					
*	*	999.5					
*	*	996.4					
*	*	996.7	997.5	1.7098			
Al	Ag	$Ni_{0.50}Co_{0.50}$					
655.1	956.8	846.8			841.9		
654.0	957.0	845.9			841.7		
653.8	956.3	846.3			841.2		
653.5	955.8	846.5	846.4	0.3775	840.8	841.4	0.4869
Al	Ag	$Ni_{0.50}Co_{0.50}$					
654.6	956.7	847.4			842.5		
654.3	958.0	846.8			843.8		
653.0	957.2	846.8	847.0	0.3464	843.2	843.2	0.6443
Al	Ag	$Ni_{0.67}Co_{0.33}$					
656.6	958.5	637.8			634.9		
655.6	958.7	637.2			635.8		
655.7	959.5	638.7			638.8		
655.1	959.4	636.8			637.4		
655.5	958.4	637.5	637.6	0.7176	635.6	636.5	1.5805
Al	Ag	$Ni_{0.67}Co_{0.33}$					
656.3	959.4	639.6			638.9		
653.9	958.2	637.2			636.6		
653.6	957.5	637.0			635.2		
653.2	957.7	638.2			637.2		
653.1	957.6	638.3	638.1	1.0383	637.2	637.0	1.3238

* Melting points were not obtained as a result of interaction between melting point standards.

Table 1 Continued

T_m^{obs}	T_m^{obs}	T_c^{obs}	T_c^{obs}avg	$T_c^{obs}\sigma$	T_c^{corr}	T_c^{corr}avg	$T_c^{corr}\sigma$
In	Zn	$Ni_{0.90}Cu_{0.10}$					
152.6	415.2	229.3			224.8		
153.6	415.0	229.1			223.5		
153.9	414.6	229.1			222.6		
153.7	413.9	228.2			220.7		
153.4	414.7	229.1	229.0	0.4336	223.2	223.0	1.5038
In	Sn	$Ni_{0.80}Cu_{0.20}$					
153.5	227.8	80.5			74.4		
152.3	227.5	79.4			74.8		
152.8	227.1	80.0			73.2		
153.1	227.9	79.8			74.8		
152.8	227.9	79.8	79.9	0.4000	75.4	74.5	0.8136

published results using pure nickel [3] and Ni–Co alloys [4]. Currently, work is underway to determine whether these unexpected results are due to instrumental effects, experimental techniques, or inherent problems with the alloys themselves.

References

1 S. D. Norem, M. J. O'Neill and A. P. Gray, Thermochim. Acta, 1 (1970) 29.
2 P. D. Garn, O. Menis and H. G. Wiedemann, Thermal Analysis, Vol. 1, H. G. Wiedemann (Ed.), Birkhauser Verlag, Basel 1980, p. 201.
3 P. K. Gallagher, Z. Zhong, E. L. Charsley, S. A. Mikkail, M. Todoki, K. Taniguahi and R. L. Blaine, J. Thermal Anal., 40 (1993) 1423.
4 B. J . Weddle, S. A. Robbins and P. K. Gallagher, Pure Appl. Chem., 67 (1995) 1843.
5 H. Preston-Thomas, Metrologia, 27 (1990) 3.
6 J. Orehotski and K. Schroder, Phys. Cond. Matter, 17 (1974) 37.
7 T. B. Massalski (Ed.), Binary Alloy Phase Diagrams, Vol. 1, ASM, Metals Park, OH, 1990, pp. 782–3.
8 P. K. Gallagher, P. T. Chao, L. Zhong and J. Subramanian, J. Thermal Anal., 39 (1993) 975.
9 P. K. Gallagher and D. A. Fleming, Chem. Mater., 1 (1989) 659.
10 P. K. Gallagher, H. M. O'Bryan, F. Schrey and F. R. Monforte, Bull. Am. Ceram. Soc., 48 (1969) 1053.