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Enthalpy measurements on a titanium modified austenitic stainless steel

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Abstract

The enthalpy values for a titanium modified, neutron swell-resistant austenitic stainless steel (D9) with a titanium to carbon ratio of about six, have been measured by drop calorimetry technique in the temperature range 295 to 1100 K. The specific heat of D9 has also been estimated from the measured variation of enthalpy with temperature.

Keywords: Austenitic steel; Calorimetry; Enthalpy

1. Introduction

Austenitic stainless steels, as a class of structural material have wide-ranging applications. In nuclear industry, especially in liquid sodium cooled fast reactors, austenitic stainless steels of type AISI-316 and its closely related variant-316 LN are the most preferred candidates for making reactor core components [1]. Apart from good high temperature mechanical, corrosion and welding properties, adequate resistance to neutron irradiation induced void swelling is a major requirement for any reactor core structural material [1]. In line with this philosophy, an austenitic stainless steel with specifically tailored composition, especially with regard to the carbon and titanium content, has been designed around the standard AISI-316 stainless steel, such that the modified grade with appropriate quantum of prior cold work exhibited improved swell-resistant properties. This titanium modified austenitic steel is designated as D9 [1]. The production history and mechanical property characterisation of an indigenous version of this alloy have already been documented [2,3]. Further, the high temperature thermal expansion behaviour of this material has also been studied by us recently [4]. Since the availability of reliable thermodynamic data is a prerequisite from the point of view of understanding phase stability, it is decided to measure as a part of an ongoing characterisation programme, the enthalpy values of an indigenously developed D9 stainless steel. The results of this study are reported in this paper.

2. Experimental details

The D9 used in this study is procured from MIDHANI, India and its composition, as determined by direct reading optical emission spectrometry, is listed in Table 1 [4]. The original material is obtained in the form of long cylindrical rods of about 2.5 cm in diameter. This is cut into smaller blocks, which are subsequently solution annealed at 1273 K under argon atmosphere for about 1 h.

The enthalpy measurements are performed with small pieces, weighing about 50 to 100 mg that are chipped from this solution annealed blocks. Each sample is precisely determined of its mass to an accuracy of 0.1 mg. The drop calorimetry measurements are performed with SETARAM-HTC 96® high temperature calorimeter.

The furnace and the experimental chamber are evacuated to start with and have been subsequently purged with argon before the commencement of each experimental run. An inert

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Table 1
Composition of D9 stainless steel used in the present study

Element	Ni	Cr	Mn	Mo	Ti	Nb	Si	C	Fe
Wt.%	14.7±3	15±0.4	1.5±0.5	2.2±0.1	0.3±0.002	<0.167	0.67±0.03	0.05±0.004	Bal.

Only major elements are listed. Besides these, the steel contains 0.009±0.001 P, 0.008±0.003 S, 0.06±0.002 V and 0.04±0.002 Co as well. Nitrogen content is not analysed in the present study.

atmosphere is maintained throughout the experiment to avoid the evaporation of carbon from the graphite furnace at high temperatures. During the preparatory stages of the drop bed, highly pure dry alumina powder is filled up to two thirds of a small recrystallized alumina crucible that is housed at the bottom of the experimental chamber. The alumina bed in turn is heated by a surrounding graphite furnace. The D9 stainless steel samples are placed in individual specimen slots, provided with the top assembly of the experimental chamber. In addition, standard samples of α-Al_2O_3, supplied by SETARAM are also loaded into the remaining slots of the specimen carousel. The temperatures of the furnace and that of the experimental chamber are independently measured by Pt–Pt/Rh thermocouples. The whole experiment, other than ensuring the drop of the sample is controlled through a computer that is connected to the main equipment through a proprietary interface module. Previously, weighed and cleaned samples are loaded in to the specimen holder which is kept at ambient temperature, namely 295 K. The furnace is then gradually heated to the desired experimental temperature under argon gas cover at a rate of 10 K per minute. Once the temperature of the alumina bed has reached the pre-set value within an accuracy of about ±1 K, the D9-samples are dropped from their respective slots through a guiding alumina tube into the hot alumina bed. The heat absorbed by the specimen upon its drop from ambient temperature into the preheated alumina bed is accurately quantified by monitoring the change in temperature of the bed as a function of time. The exercise is repeated with α-Al_2O_3 standards under identical conditions. Assuming negligible heat loss due to radiation

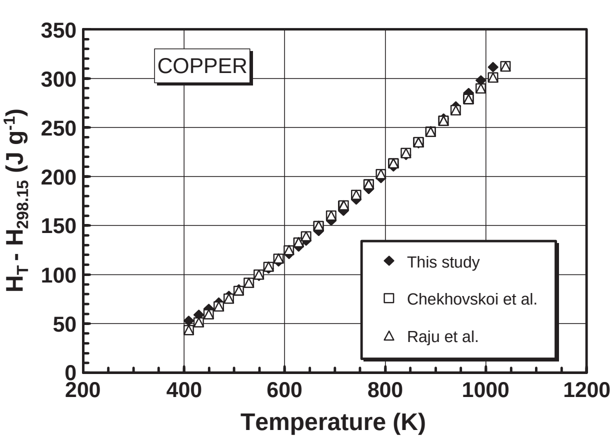

Fig. 1. Enthalpy increment values obtained for copper in the present study are compared with data taken from the literature. Note that the latest data due to Chekhovskoi et al. [7] are based on drop calorimetry measurements, while that of Raju et al. are arrived at by using an integrated data assessment procedure [8].

and besides, invoking quasi-adiabatic conditions to prevail in the experimental chamber, Q_S (T), the heat energy transported from the bed to the sample may be written as follows [5].

$$Q_S(T) = C(T)(m_S/M_S)(H_T - H_{295})_S. \quad (1)$$

In Eq. (1), m_S is the actual mass of the sample, M_S its molar mass, H_T–H_{295} is the measured enthalpy increment with respect to 295 K and C is a temperature dependent calorimeter constant. The latter quantity may be obtained from the heat change measured with respect to the alumina reference (Q_R) and from a knowledge of its critically assessed enthalpy values [6]. Thus,

$$Q_R(T) = C(T)(m_R/M_R)(H_T - H_{295})_R. \quad (2)$$

In the above expression, m_R and M_R denote respectively the actual and the molar mass of alumina reference, which is taken to be 101.96 g mol^{-1}. For D9, the enthalpy values are measured at 35 individual temperature intervals in the range 360 to 1100 K. A minimum of two runs are performed at each temperature with samples of slightly different mass. It is found that these two values show a fair degree of agreement for temperatures exceeding 450 K. For lower temperatures, the quantity of heat transported being rather small, a comparatively large scatter is seen. At temperatures higher than about 1100 K, the alloy D9 samples showed mild signs of oxidation. This is also evident from the recorded heat flow versus time profile in that, a very shallow endothermic trough is seen superposed over and above the otherwise smooth exponential rise that is characteristic of temperatures lower than 1100 K. However, in the present study, we also measured the enthalpy of OFHC grade copper (better than 99.9% pure) up to a temperature of 1100 K. These values are compared against the reported ones in the literature [7–9]. A good agreement is obtained between the values measured in the present study and the reported ones [7–9], including the latest assessment by the present authors [8]. This is illustrated in Fig. 1. The extent of deviation of the measured enthalpy values of copper from the latest experimental results of Chekhovskoi et al. [7] is made use of in arriving at an empirical correction factor, that is subsequently applied to the raw enthalpy data of D9 to obtain corrected enthalpy estimates.

3. Results

In Fig. 2, the measured enthalpy values for D9 are plotted together with the currently available experimental enthalpy

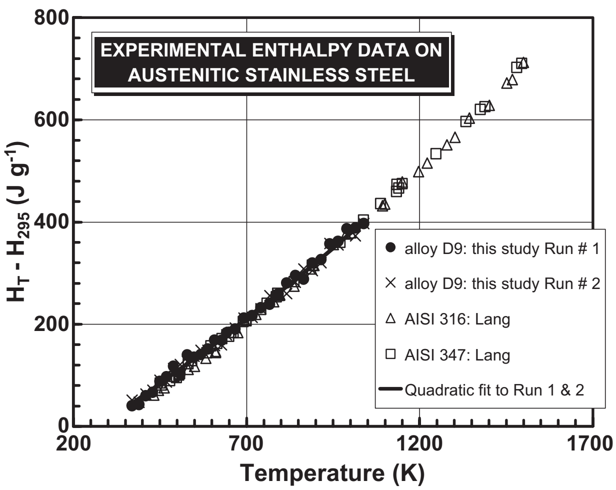

Fig. 2. Enthalpy increment data obtained in the present study for D9 are compared with the extant experimental data on type 316 and 347 steels [12].

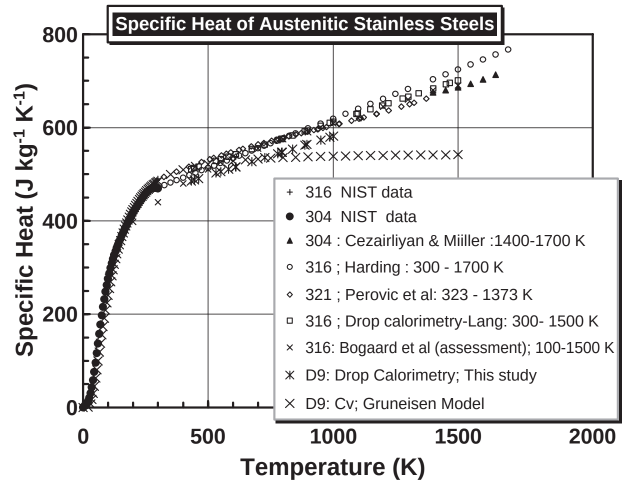

Fig. 3. The measured C_P values for D9 are compared with the literature data on other related austenitic stainless steels.

data on AISI-316 and 347 stainless steels [10,11]. It is clear that the enthalpy values obtained in the present study for D9 are in excellent agreement with these data on related grades. Before proceeding further, it must be mentioned that to the best of our knowledge, we are not aware of any information on experimentally determined enthalpy data on D9. The enthalpy increment (H_T-H_{295}) data corresponding to two distinct experimental runs are fitted to a second-degree polynomial in temperature increment ($T-295$). The resulting expression is given below.

$$H_T - H_{295} = 9.996 + 0.4621(T - 295) + 8.466 \times 10^{-5}(T - 295)^2. \quad (3)$$

In Eq. (3), H_T-H_{295} is given in J g^{-1} and temperature T, in K. Further, Eq. (3) is found to fit the experimental data with an R^2 value of 0.995 in the temperature range 370 to 1100 K. At this juncture, a question may arise as to the value of the intercept given by Eq. (3), in that it is expected to be zero identically. In this regard it must be stated that Eq. (3) represents a constrained fit to the actual experimental data in the sense that the derivative of enthalpy increment at 295 K as given by Eq. (3), is made to agree with the estimated C_P for this alloy, namely 462 J kg^{-1} K^{-1}. This latter value corresponds to the experimentally obtained C_P for 316 stainless steel [11]. The choice of this value for D9 may be justified as follows. In general, it may be remarked that the thermal properties of closely related austenitic stainless steels do not show much of a variation to the first order of approximation [11]. In the light of this situation, it may be said that in the absence of reliable experimental data for a new candidate in the austenitic steel family, the value corresponding to a well-studied homologous member of this family may be taken as a good representative of the entire class itself. It is in this spirit,

Table 2
Listing of experimentally measured enthalpy increment and specific heat values for D9 stainless steel at select temperatures

T (K)	H_T-H_{295} (J g^{-1})			C_P (J kg^{-1} K^{-1})	T (K)	H_T-H_{295} (J g^{-1})			C_P (J kg^{-1} K^{-1})
	Run 1	Run 2	Fit to Eq. (3)			Run 1	Run 2	Fit to Eq. (3)	
409.3	60	63	64	481	716.8	217	213	220	534
429.2	67	71	74	485	742.0	232	230	233	538
449.4	88	90	83	488	766.7	239	255	247	542
489.1	118	113	103	495	791.6	259	257	260	546
528.8	140	127	123	502	816.0	281	260	274	550
548.6	135	137	133	505	841.0	295	282	288	555
568.4	140	149	143	508	865.3	288	308	301	559
588.1	151	149	153	512	890.3	320	305	315	563
608.2	169	158	163	515	915.2	326	320	329	567
627.8	168	159	173	518	940.1	357	358	343	571
642.9	183	179	181	521	964.8	362	355	357	576
667.6	190	192	194	525	989.6	387	376	372	580
692.4	212	212	207	529	1014.1	388	373	386	584
					1038.9	397	397	401	588

The enthalpy and specific heat values are rounded of to the nearest integer.

we have chosen a trial value for the C_P of D9 at 295 K. In Table 2, the enthalpy and the C_P data estimated using Eq. (3) are presented. In Fig. 3, the C_P values of D9 obtained from enthalpy data are compared with the limited information on austenitic stainless steels that is gleaned from the literature [12–17].

It is heartening to note that the present estimates are by and large in accord with the expected trend. It is also clear that C_P of austenitic stainless steels in general exhibit a steady rise up to the melting point, a trend shared by the corresponding thermal expansion data as well [4]. In fact, it may safely be assumed that the ratio of thermal expansivity to specific heat is only weakly temperature dependent in these steels. Based on this assumption, we made an attempt to estimate the vibrational contribution to C_V of D9 using such information as measured thermal expansion data, room temperature Grüneisen parameter and bulk modulus. Although these values are yet to be determined for D9, a rough estimate is however possible based on homologous behaviour among austenitic steels. The details of this modelling are elaborated in our earlier publication concerned with the thermal expansion of D9 [4]. The result of this calculation is also plotted in Fig. 3. It is clear that notwithstanding the assumptions involved, a Grüneisen type modelling captures the essence of the thermal property behaviour in D9.

4. Conclusion

The enthalpy of a titanium stabilised austenitic stainless steel, namely D9 has been measured by drop calorimetry technique in the temperature range 300–1100 K. The measured enthalpy values are found to be of the same order of magnitude as the reported ones for other related grades of austenitic stainless steels.

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