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Calorimetric Study of Eutectics: Solid Solubility Limit and Entropy of Fusion of Either Phase

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Melting of pure metals and metallic eutectics imply invariant reactions. The thermal characteristics recorded by DTA technique are well suited for adjusting a DTA apparatus for differential scanning calorimetry (DSC).

A pseudobinary cut in the system Co-Cr-C from Co - 29 wt.pct. Cr to Co - 41 Cr - 2.4 C was investigated to yield following results:

- Maximum solubility of C in metal matrix
- Heat of fusion of matrix and of carbide
- Entropy of fusion of matrix and of carbide.

Introduction

Many eutectics can be processed by means of directional solidification into composite materials [1]. The generation of natural composites out of eutectics will work if a coupled growth of the eutectic phases in the direction opposite to the heat flow is accomplished (fig. 1). One criterion for coupled growth of eutectics along a thermal gradient says that the entropy of fusion of the phases must not differ too much and must not be too high [2]. The entropy of fusion of metallic solutions is conveniently between 1 and 2. Fig. 2 shows the entropies of fusion after Hunt and Jackson in binary eutectic systems with respect to coupled growth (open cycles). The more the entropies of fusion differ the more it is less likely that aligned structures are formed. The intention of this report is to discuss the suitability of the above mentioned Co-Cr-C eutectic 73C [3] for hypothetical application as a turbine blade material in the light of solubility and growth characteristics.

Experimental Procedures

Fig. 3 represents a schematic of the DTA apparatus. 0.05 mV were plotted as 250 mm on a recorder, the chart speed was 240 mm/h. The heating rate was 5 K/min. The weight of the samples was 0.8 g. The crucibles out of 99.7 % aluminia were of uniform size and of uniform weight. The round bottom of the crucible gives a good contact between aluminia and the spherical samples. The samples were premelted in the crucibles under high vacuum to guarantee optimum homogeneity and thermal transport conditions.

The DTA-DSC experiments were carried out under argon at normal pressure, the argon was purified by hot tantalum. The passage of argon through the tube-type furnace was 0.2 l/h. The reference material was 0.5 g bulk aluminia.

The thermocouples were calibrated by melting high purity silver, copper, nickel, and cobalt. These four metals were also used to facilitate a caloric calibration of the DTA apparatus. The peak area recorded during melting of the four calibration elements is shown schematically in fig. 4. This peak area is in some proportion to the latent heat of fusion (fig. 5). But it decreases with increasing temperatures. In other words: the thermal sensitivity of the apparatus is lessened by increasing temperatures. The reciprocal thermal sensitivity of the apparatus versus temperature gives a quasi-linear relationship for the temperature range investigated (fig. 6). The slope of the straight lines in fig. 5 is also a function of temperature (fig. 7). The variation of the slope angle versus temperature has to be determined to allow a correlation between peak area and latent heat of fusion at any temperature. Figs. 6 and 7 allow to calculate peak areas as shown in fig. 8 which may represent any heat of fusion. Now the latent heat of fusion per unit weight can be calculated in cal/g. Fig. 8 shows the hypothetical peak area per 50 cal for 4 invariantly melting alloys (PdNi 60:40 melting at 1232 °C, PdCr-eutectic at 1306 °C, CoTa-eutectic at 1296 °C, 73C eutectic after [3] melting at 1303 °C) and for four alloys having a small melting interval. Now the adequate heat of fusion of the appropriate samples can be determined. The first locus is the true peak area originated by the sample, the second locus is the line through the given points at 50 cal having the appropriate slope taken from fig. 7.

Results

Six alloys along the quasi-binary cut between γ-Co and Cr_7C_3 were chosen and their enthalpies of fusion determined. Fig. 9 shows the measurements versus wt.pct. carbon. At about 0.3 wt.pct. C a minimum emphasizes the point of maximum solubility of carbon in a γ-matrix at eutectic temperature.

These results suggest that a metallic matrix of 0.3 wt.pct. C in solution is in equilibrium with Cr_7C_3 solid solution at eutectic temperature and that the heat of fusion of a eutectic alloy is an addition of the amounts of entropies of either phase.

Now the enthalpy of fusion of the carbide can be estimated graphically in fig. 9 by extrapolation of the line up to Cr_7C_3. Alternatively the volume fraction of the carbides within the eutectic can be determined. It is 30.1 %. The weight percentages of the phases can be found out by introducing the densities of the phases (Table). Now the weight percentages of the phases have to be correlated with the appropriate entropies of fusion which summarize to the comprehensive amount of heat of fusion of the eutectic. The enthalpies and entropies of fusion can now be given for either phase:

Table

$$\left.\begin{array}{ll}\text{density of }\gamma\text{-matrix} & :8.4\ \text{g/cm}^3\\ & \\ \text{density of }(Cr,Co)_7C_3\text{ carbide} & :6.9\ \text{g/cm}^3\end{array}\right\}\begin{array}{l}30.1\ \text{vol.pct. carbide}\\ =26.155\ \text{wt.pct.}\\ 69.9\ \text{vol.pct. matrix}\\ =73.845\ \text{wt.pct.}\end{array}$$

Enthalpy of fusion of the eutectic of 84.3 cal/g represents
enthalpy of fusion of γ-matrix of 30.13 cal/0.73845 g plus
enthalpy of fusion of carbide of 54.17 cal/0.26155 g.

phase	enthalpy of fusion [cal/g]	g·atom	$\frac{\text{cal}}{\text{g·atom}}$	S_M[K]	entropy of fusion $[\frac{\text{cal}}{\text{K·g·atom}}]$
γ-matrix Co-30.5 wt.%Cr -0.3 wt.%C	40.8	55.9982	2284.727	1733	1.32
carbide Cr_6CoC_3	207.1	40.6942	8428.216	2060	4.09

This generation of thermodynamic values is based on some simplifications, i.e. the specific heat does not alter at the transition temperature of the phases considered.

Conclusion

Experiments show that the solubility limit at eutectic temperature can be determined by DSC. DSC also works out to be a reliable tool for generating thermodynamic values for invariantly melting one- and two-phase alloys and for alloys having a melting range. These findings are of great concern for judging the applicability of high temperature eutectics as a convenient structural material. The variation in solubility of carbon versus temperature is found to be very low and shows therefore some promise of good temperature cycling characteristics of this material.

The entropies of melting of~1.3 and~4 differ very much. That means that only weakly coupled growth of the eutectic phases occurs. The shape of the dendrite-type carbide fibres in aligned structures cannot be changed fundamentally to fibres of uniform cross section because this change would imply a fundamental change in the growth kinetics. Therefore ideal mechanical composite characteristics cannot be expected from this family of eutectics because of the inevitable shape instabilities of the carbide fibres.

References

[1] Kurz, W.; Sahm, P.R.: Gerichtet erstarrte eutektische Werkstoffe. Ed. W. Köster, Bd. 25 Springer-Verlag 1975.

[2] Hunt, J.D.; Jackson, K.A.: Trans. Met. Soc. AIME 236 (1966) 843-52

[3] Thompson, E.R.; Lemkey, F.D.: Metallurg. Trans. 1 (1970) 2799-2806

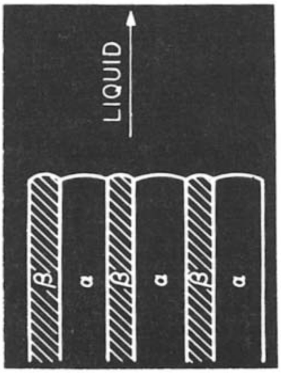

Fig. 1: Coupled growth concept of two-phase eutectic

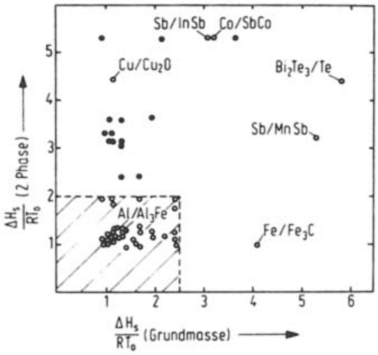

Fig. 2: Entropy of fusion of phases in binary eutectic systems (coupled growth = open cycles after Fisher and Kurz in [1])

Fig. 3

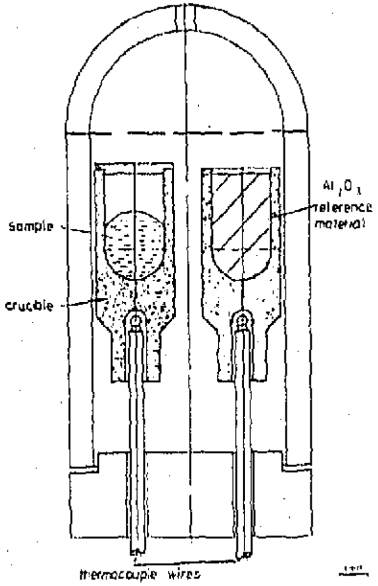

Fig. 4

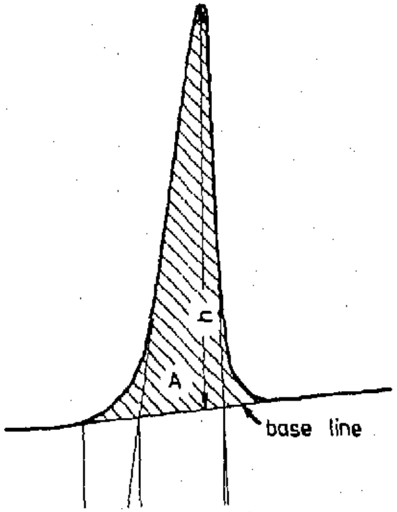

Fig. 5

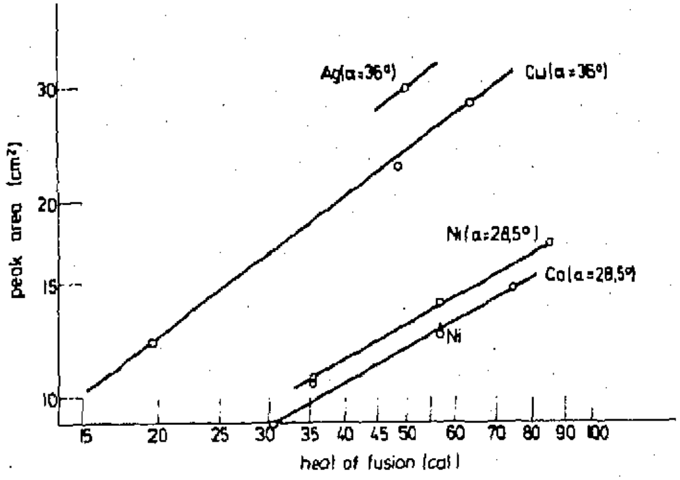

Fig. 6

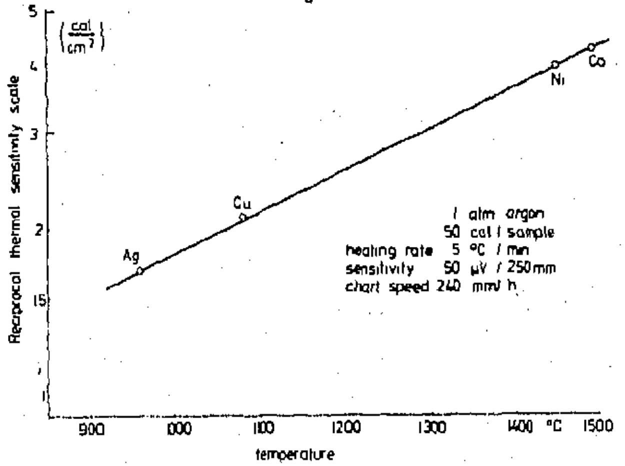

Fig. 3: Schematic of DTA apparatus

Fig. 4: Peak area (schematic) for melting

Fig. 5: Peak area vs. Latent heat of fusion for samples of Ag, Cu, Ni, and Co

Fig. 6: Reciprocal thermal sensitivity of DTA apparatus vs. temperature

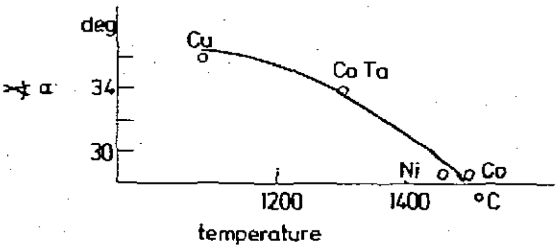

Fig. 7: Slope of lines from fig. 5 vs. temperature

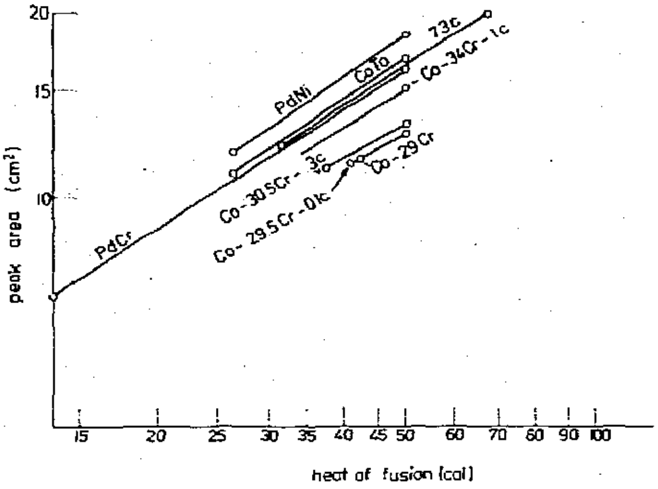

Fig. 8: Latent heat of fusion as function of temperature-dependent slope α from fig. 7 and peak area

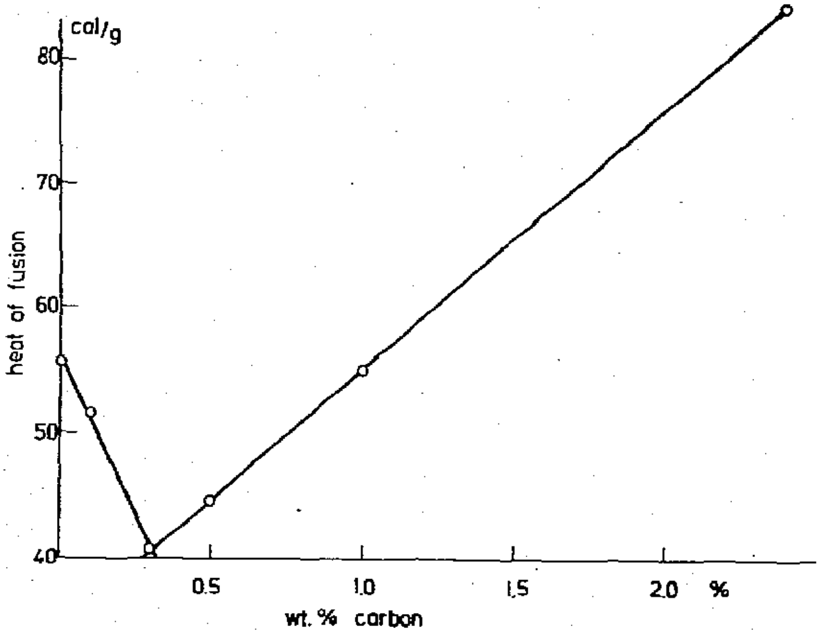

Fig. 9: Heat of fusion vs. wt.pct. carbon from Co-29% Cr to 73C (Co-41%Cr-2.4%C)