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LOW TEMPERATURE HEAT CAPACITIES OF SEVERAL HIGH STRENGTH MATERIALS

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ABSTRACT

Low temperature calorimetric measurements have been made on three metallurgically prepared high strength materials: NiAl, W-2 (a heavy tungsten alloy), and Al-Fe-Ce (a lightweight alloy with dispersion strengthening). To fit the heat capacity data between 3 and 10³K, not only the electronic and lattice contributions having T and T³ dependence, respectively, need to be considered, there is an additional temperature-independent term presumably associated with magnetic clusters. These results provide information on the fundamental characteristics, as well as the heterogeneous nature of the materials not always detectable by standard metallurgical techniques.

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INTRODUCTION

The ever increasing demand of high strength materials for a wide range of applications has led to the advancement of many special manufacturing technologies. Among them the powder metallurgy is particularly attractive. This method allows almost any conceivable alloy systems to be synthesized under equilibrium or nonequilibrium conditions. With alloying elements dispersed throughout one another to achieve specially designed microstructures, the resulting materials often exhibit excellent mechanical properties. Furthermore, powder metallurgy simplifies processing steps and helps form high strength parts of complicated configurations at much reduced difficulty and cost.

This work deals with low temperature calorimetric studies of three high strength materials synthesized by powder metallurgy: NiAl, W-2, and Al-Fe-Ce.

In the rather wide composition range of 45 to 60 atomic % Ni of the Ni-Al binary system, an intermediate phase β' based on NiAl has a CsCl structure. The intermetallic compound NiAl has been the subject of many materials research programs¹ because of its structural stability at high temperatures. The sample used has a Ni content of 49.3 wt%. W-2 contains tungsten grains mixed with 2.7 wt% of Fe/Ni/Cu particles.* Extensive quality control in initial powder production ensures a consistent, homogeneous as-sintered matrix with virtually no porosity. This material has a good machinability and, like most tungsten base alloys, has a high weight-to-volume ratio required in certain applications. In contrast, Al-Fe-Ce represents a new type of lightweight aluminum alloys with dispersion strengthening. Our sample contains 8 and 4 wt% of Fe and Ce, respectively.²

EXPERIMENTS AND RESULTS

Heat capacity measurements were made between about 3 and 10°K with an adiabatic calorimeter. Pulsed, electrical heating and germanium thermometry were used. The heater and the thermometer were attached to a copper block, which was in turn thermally anchored to the sample weighing 20 to 40 g each. Heat capacity of the copper block in the same temperature range was separately determined for addenda corrections.

The low temperature heat capacity of a typical, metallic solid can be expressed as a function of temperature:³

$$C = \gamma T + \beta T^3.$$

The linear term is associated with conduction electrons, with its coefficient γ related to the density of states at Fermi level. The T^3 -dependent term arises from lattice vibrations. The coefficient β is proportional to θ_D^{-3} , where the Debye characteristic temperature θ_D is a measure of the bonding strength of the lattice. Accordingly, a plot of C/T versus T^2 should yield a straight line as shown by the data for pure aluminum in Figure 1. However, this is obviously not the case for the Al-Fe-Ce sample. Rather, a third, temperature-independent contribution to heat capacity needs to be included to fit the data:

$$C = A + \gamma T + \beta T^3.$$

This allows again a linear fit for $(C-A)/T$ versus T^2 . Similar results are obtained for NiAl in Figure 2 and for W-2 in Figure 3, where the normal behavior of pure tungsten⁴ is also exhibited for comparison. Whereas the γ value of NiAl is the same as that obtained by Seitchik and Walmsey⁵ from a sample showing no temperature-independent term in heat capacity, the β value corresponds to a Debye temperature of 470°K, which is much lower than their value of 560°K.

*W-2 is a heavy tungsten alloy developed by Kennametal Inc. for aerospace and nuclear industries.

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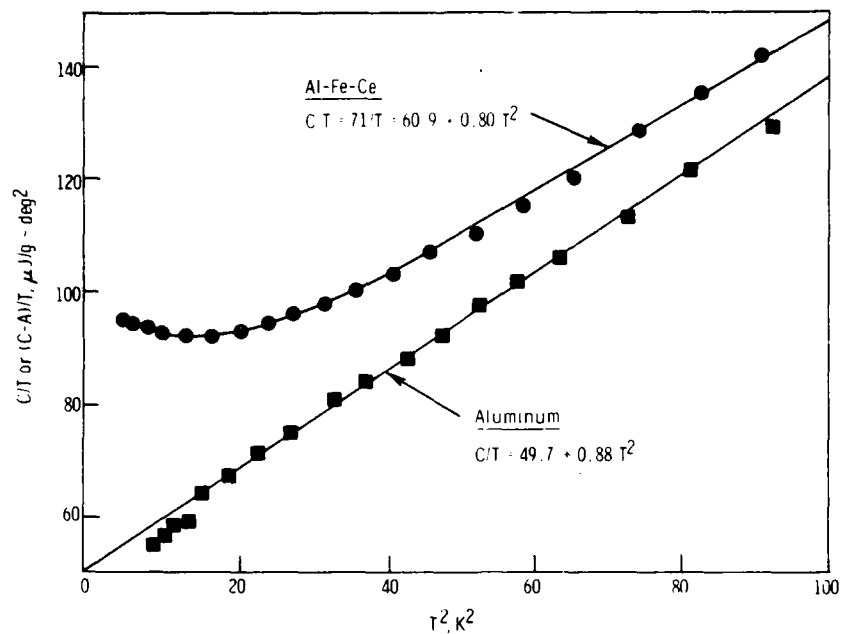


Figure 1. Low temperature heat capacities of pure aluminum and Al-Fe-Ce alloy.

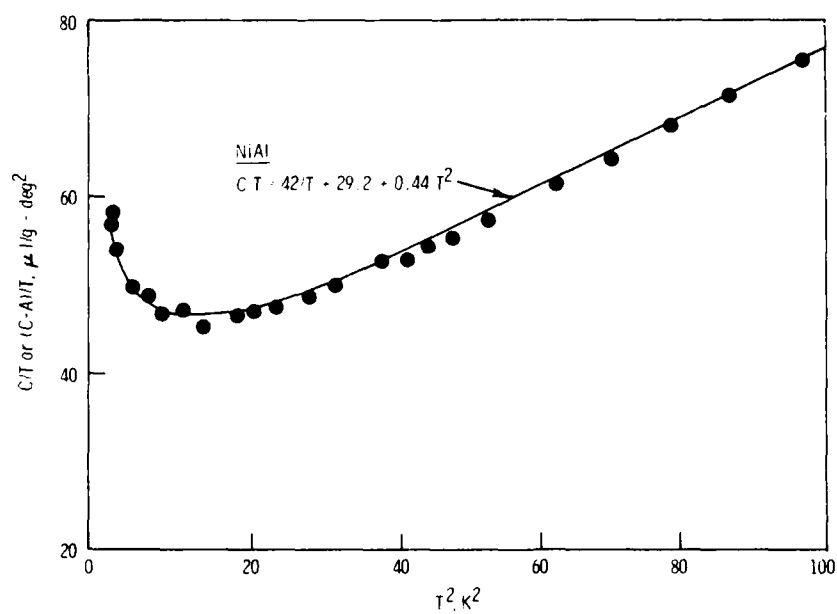


Figure 2. Low temperature heat capacities of NiAl.

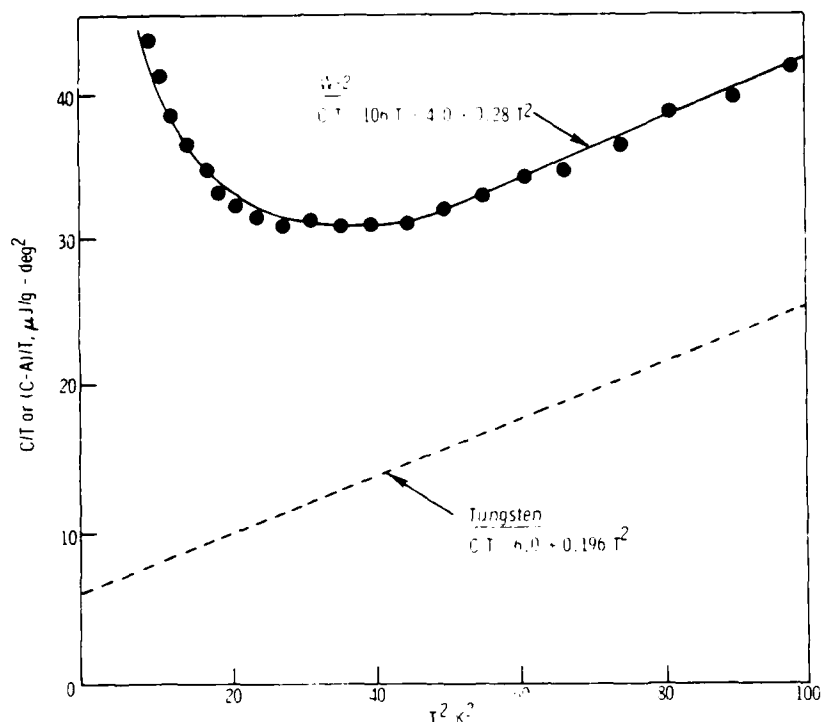


Figure 3. Low temperature heat capacities of pure tungsten and W-2 alloy.

It should be noted that, while a homogeneous NiAl is of a single phase, the other two samples have Al or W matrix with the additional elements Fe/Ce or Fe/Ni/Cu present as dispersed particles of different phases for mechanical properties enhancement. In this regard, the calorimetrically determined γ and β values for the multi-phase materials represent only average values and their differences from those for the matrix materials are considered reasonable in magnitude.

DISCUSSION

Temperature-independent heat capacities have previously been observed in other materials at low temperatures, following the first report on TiFe by Schroder and Cheng⁶ in 1960. These materials invariably contain magnetic elements Fe, Co, or Ni, but are not magnetically ordered. The interpretation,* which is likely valid here, involves the clustering of such magnetic elements on a submicroscopic scale not always detectable with standard metallurgical techniques. In principle, energy levels of magnetic clusters with spin J can be split by crystalline anisotropic effects.⁶ The resulting energy level pattern produces a specific heat anomaly, i.e., in these crystal extra degrees of freedom lead to a constant heat capacity contribution if the thermal energy is much greater than the energy associated within interaction between the magnetic moments of the clusters and the crystal field. Such a condition is apparently satisfied in this work even at relatively low temperatures.

Clustering occurs when atoms of the same kind tend to associate together. This and the short-range ordering reflect deviations from either an ideal solid solution or a superlattice. Studies of their occurrence are of importance towards a better understanding of alloys in general. In this regard, it is of interest to reveal, through low temperature calorimetry, the existence of clusters not only in W-2 as somewhat expected, but also in NiAl and the

*For detailed discussion, see R. L. FALGE, Jr., and N. M. WOLCOTT. *J. Low Temp. Phys.*, v. 5, 1971, p. 617.

6. SCHRODER, K., and CHENG, C. H. *Correlation of Low-Temperature Caloric and Magnetic Effects in TiFe*. *J. Appl. Phys.*, v. 31, 1960, p. 2154.

Al-Fe-Ce alloy. Furthermore, the non-zero temperature-independent A-term in heat capacity and the lower Debye temperature of our NiAl sample, as compared to that of Seitchik and Walmsey⁵ may very well be closely related since A is related to cluster per mole or inhomogeneity in the material. The possible effect of clusters on the performance of high strength materials like W-2, as well as the dependence of their formation on manufacturing processes should, therefore, be systematically investigated by performing similar measurements on W-4, W-6, and W-10 where the alloying elements Fe/Ni/Cu are present in 4, 6, and 10 percent by weight, respectively, in tungsten.

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