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no

AECU-3556

PHYSICAL METALLURGY OF UNCOMMON METALS

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Date of Issue: May 15, 1957

Contract No: AT(30-1)-981

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Physical Metallurgy of Uncommon Metals

Introduction

The work described in this report was carried out by Massachusetts Institute of Technology personnel under the supervision of Professors John T. Norton, Robert E. Ogilvie and Albert R. Kaufmann during the fiscal year 1956-57. The magnetic work was carried out by Mr. S. T. Lin and the structure work by Dr. Erwin Parthe in laboratories at the Institute. The work by Dr. Stanley Gelles was done at Nuclear Metals, Inc. and is based on part of a thesis submitted by Dr. Gelles in partial fulfillment of the requirements for the Doctor of Science degree.

Magnetic Research

by S. T. Lin

The progress of magnetic research, can be briefly summarized in the following three sections.

I. Development of a Cryostat

A new cryostat made of all metal has been developed. In the near future it will be put into operation. This cryostat is based on the principle of utilizing the liquid helium gas to cool a massive coil of copper tubing which in turn cools the guided tube and the working space. The temperature is controlled by the pumping speed of the helium gas through the copper coil. The cryostat can produce any intermediate temperature between liquid nitrogen and liquid helium for long periods of time. This achievement can make possible the investigation of the magnetic properties in this intermediate temperature range in detail.

II. Magnetic Susceptibility of UMn_2

The magnetic properties of UMn_2 have been thoroughly investigated from 360°K to 4.2°K. The magnetization curves for the complete range of temperatures have been determined. From these data it has been found that there are three unusual magnetic phenomena which are characteristic of this new material.

a. From 77°K to 360°K the curve of susceptibility against temperature (Figure 1) shows a broad maximum around 260°K which suggests that UMn_2 is probably an antiferromagnetic material.

(In the near future we may have a chance to confirm this characteristic by neutron diffraction.)

b. At liquid helium temperature the susceptibility increases almost double to the value of those above liquid nitrogen temperature. This phenomenon is not uncommon. Metallic manganese itself and dilute alloys of nickel in copper also show this low temperature anomaly but the interpretation is still quite controversial.

c. The material shows a small remanence and magnetic hysteresis shift. As this is an entirely new phenomenon it would be better to describe it a little more in detail.

III. Magnetic Hysteresis Shift of UMn_2 , CoO and UH_3

For ordinary ferromagnetic material the magnetic hysteresis loop is symmetrical with respect to the origin. More than a year ago we found in this laboratory that for UMn_2 the small remanence, the coercive force and the maximum magnetization (the two tips) of the hysteresis loop are all asymmetric with respect to the origin if the temperature of the sample is well below its transition temperature. In the past six months we have studied this new phenomena and considerable and reliable data have been taken. It has been found that there are at least two different kinds of shifts -

1. Shift along the magnetization axis (vertical axis) of the hysteresis loop only. For this kind of shift the whole hysteresis loop can be made entirely symmetrical by adjusting the vertical axis only.

2. Shift along both the vertical and the horizontal axis (field axis). For this kind, the loop cannot be made entirely symmetrical without adjusting both axes.

a. UMn_2 - This material belongs to the first kind. It shows hysteresis shift not only when cooled in magnetic field but also when cooled without field although in case of cooling without field the shift is smaller than that for the other case. As no complete hysteresis loop of antiferromagnetic material has been reported in the literature a few of the loops (Figures 2, 3 and 4) are attached to show the general forms. All the loops were determined when the sample was cooled in magnetic field about 7000 Oe. It is very interesting to note that at very low temperature especially at helium temperature the whole loop (Figure 4) shifts to one side of the origin. This means that once the material is magnetized it cannot be demagnetized no matter how strong the demagnetizing field, it can only be demagnetized by heating the material above its transition temperature. Figure 5 shows the shift of coercive force against temperature. The curve cuts the temperature axis at about 180°K. At this temperature the hysteresis loop is symmetrical and the loop area is at its maximum value. This temperature may be significant.

b. CoO - CoO is another anti-ferromagnetic material. The transition point is about room temperature. Below liquid nitrogen temperature the magnetization curve shows no remanence and the susceptibility is field independent. At liquid helium temperature however it shows a small remanence and the hysteresis loop area is almost reduced to zero (Figure 6). The loop almost degenerates into a straight line which does not pass through the origin.

c. UH_3 - This material is a ferromagnetic compound. It shows hysteresis shift when cooled in magnetic field (Figure 7). This shift belongs to the second kind because the loop can only be made symmetrical by adjusting both axes.

Very recently Meiklejohn and Bean of General Electric Company published a paper (Phys. Rev. 105, 904 (1957)), entitled "New Magnetic Anisotropy". In this paper it was claimed that the sample CoO (metallic powdered cobalt coated with cobaltous oxide) showed asymmetric hysteresis when the sample was cooled in a magnetic field. As metallic cobalt is ferromagnetic and cobaltous oxide is anti-ferromagnetic they proposed a theory that this shift is due to ferromagnetic and anti-ferromagnetic interaction which introduces an unidirectional magnetic anisotropy. The above described phenomena which we have found does not seem to support their theory because pure anti-ferromagnetic material UMn_2 and CoO and pure ferromagnetic material UH_3 have no ferromagnetic and antiferromagnetic interaction. Recently, L. Niel and Y.Y. Li proposed an anti-ferromagnetic domain theory. In this theory an unbalanced domain wall magnetization was suggested. This magnetization may explain the small remanence of UMn_2 and CoO . As the coupling of anti-ferromagnetism is very strong especially at very low temperature, the magnetization shows unidirectional character. This suggestion however, is still unable to explain the material UH_3 except that UH_3 is supposed to be a kind of ferrimagnetic material. Meiklejohn and Beans' data is incomplete. Their hysteresis loop has no data points, their units are arbitrary and their readings

only refer to liquid nitrogen temperature. We have no way of making a comparison with our data.

As this discovery opens a new field in magnetism and is important in theory and application, it would be advisable to do more survey work to determine which kinds of material show this effect and in which temperature range the effect is prominent. After such experiments have been done, the interpretation would be much easier and more reliable. Since the material, which shows this effect, usually has high coercive force and it needs a long time (4 to 8 hours) to keep the material at very low and constant temperature in order to finish the whole hysteresis loop, our special and powerful magnet combined with the newly developed cryostat seems to be the unique instrument which can be used to study this new phenomenon.

UMn₂
 TEMPERATURE 123.85 °K
 FIG 2

UMn₂
 TEMPERATURE, LIQUID NITROGEN
 FIG. 3

UMn₂
 TEMPERATURE, LIQUID HELIUM
 FIG. 4

The Zr-Si-B System

by Erwin Partha

The object of this program has been to study the phase diagram and the structure of intermetallic phases in the ternary system Zr-Si-B. In order to prepare the high melting samples, a hot press (20V, 4000A) for temperatures up to 2600°C was put in operation. This included the construction of a continuous regulating inductive resistor for 5000A. Furthermore, some thermodynamic calculations were made to find a crucible material which would not react with C, B and liquid Si at 2200°C. This led to BN which was found experimentally suitable as a crucible material for Si and B melts.

Binary Systems

Zr-B - In accordance with previous investigations, three intermetallic zirconium borides have been found; ZrB, ZrB₂ and ZrB₁₂. The lattice constants are in agreement with the reported values.

Zr-Si - The phases ZrSi₂, ZrSi and Zr₅Si₃ have been found. No efforts have been made to prepare more metal rich zirconium silicides as only specially purified zirconium must be used for the preparation of this compound. Small amounts of oxygen or carbon (0.2 at. % C) favor the formation of a ternary silicide Zr-Si-O (C,N) with D8₈ structure, the so-called Nowotny-phase which masks all other pure metal rich zirconium silicides. It has been shown also that a small boron addition of 5 at. % stabilizes this ternary phase.

Si-B - It has been experienced that even at 2000°C there is no reaction between B and Si. In the case of a carbon container, the only phases formed are B_4C or SiC . Melts of B-Si mixtures at 2200°C in BN crucibles revealed a crystallized shiny material which contained elementary Si and a silicon boride. It has been found that the silicon boride is resistant to ice-cold $HF-HNO_3$ mixtures but will dissolve in heated $HF-HNO_3$ mixtures. Thus a method to separate Si from silicon boride was developed. It was possible to make a Weisenberg photograph with a tiny crystal of the silicon boride. The preliminary data of the new compound are listed in the following table.

Composition:	SiB_{12}
Melting point:	Probably 2200°C
Density:	1.72 g/cm ³
Crystal Structure:	Rhombic with $a = 11.10$ Angstroms $b = 14.79$ " $c = 10.12$ "
Chemical Properties:	Insoluble in cold $HF + HNO_3$ Soluble in hot $HF + H_2SO_4$
Appearance:	Metallic, high brilliance, crystals with no preferred crystal form.

Ternary System

In the ternary system there exists one ternary compound near the Zr-Si side. This compound is a Nowotny phase with $D8_g$ structure, which is stabilized with about 5 at. % B. It was possible to find an empirical stability law for Nowotny phases of the form atomic percent metalloid = $25 \left(1 - \frac{K}{N}\right)$ where K is a constant and N is the group number of the metal component. This law was proved on C

stabilized Nowotny phases and should hold for B stabilized Nowotny phases. The following table shows calculated and observed compositions of C stabilized Nowotny phases.

Composition of C Stabilized Nowotny Phases							
	4th group		5th group		6th group		
	K	Obs.	Cal.	Obs.	Cal.	Obs.	Cal.
4th period	4.0 ₀	0	0	1-?	5	5-10	8.2
5th period	3.7 ₅	0.3-4.0	1.5	3-28	6.2	9-16	9.4
6th period	3.3 ₅	?	4	5-10	9		(11)

The given empirical relation may be traced back with a given reserve to the electron concentration of the metal remaining in the 4d position of the $D8_8$ structure. Details may be studied in "Contributions to the Nowotny Phases" by E. Parthe, Powder Metallurgy Bulletin 1957. The ZrB_2 with the AlB_2 structure shows considerable solubility for $ZrSi_2$ that almost a filled $NiAs$ structure is reached at the homogeneity limit. This is also the case with the isotype $ZrBe_2$ and $ZrBeSi$. The accurate shape of the $Zr(B,Si)_2$ homogeneity range has to be determined in more detail.

The distribution of the phase fields in the Zr-Si-B system were calculated by the method given by Brewer. The experimental results which agree with the calculations, are given in the attached diagram.

Conclusions

Three results of this work are of certain technical interest.

1. ZrB_2 dissolves a certain amount of $ZrSi_2$. $Zr(B,Si)_2$ alloys should be tested for their oxidation resistance. The formation of a boron silicate glass during oxidation is probable.

2. The compounds in the Si-B system have to be tested for their properties. No useful predictions are available.

3. BN is a promising crucible material. The possibility of melting boron without difficulty is of considerable importance in the preparation of boron containing alloys.

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Preliminary Section at 1350°C

Solubility Limits and Diffusion of Iron and Nickel
in Beryllium Primary Solid Solutions

by Stanley H. Gelles

The solid solubility limits of iron in beryllium were determined between 850°C and 1200°C by analysis of differential type multi-phase diffusion couples using an x-ray absorption technique. The maximum value of the solubility limit was found to be 0.920 atomic percent (5.46 weight percent) at the eutectic temperature, 1225°C. The solubilities of nickel in beryllium were determined between 900°C and 1200°C by the same technique and the maximum solubility was found to be 4.93 atomic percent (25.2 weight percent) at the eutectoid temperature, 1065°C.

A previously unreported high-temperature phase (designated β in this work), which decomposes eutectoidally at 1065°C was found to exist in the beryllium-nickel system at a composition of approximately 8 atomic percent nickel (36 weight percent) by diffusion couple analysis. The presence of this phase was confirmed by thermal analysis and metallographic analysis of the structures resulting from the eutectoid decomposition.

Interdiffusion coefficients were determined as a function of composition and temperature for the beryllium-iron and beryllium-nickel primary solid solutions by means of a Matano-Boltzmann analysis of the concentration gradients obtained in the differential diffusion couples. The diffusion coefficients show a slight tendency of increasing with alloy content but the variation is small enough to be neglected. The diffusion coefficient for a given temperature may then be represented as its average value for the composition range investigated.

The variation of the average interdiffusion coefficient ($\bar{D}$) with absolute temperature (T) can be represented for these systems as:

$$\bar{D}_{\text{Be-Fe}} = 1.3 \exp \left[-54.0 \times 10^3 / RT \right]$$

$$\bar{D}_{\text{Be-Ni}} = 0.11 \exp \left[-47.2 \times 10^3 / RT \right]$$

Interdiffusion coefficients were also calculated for these primary solid solutions by a method after Wagner and Jost which traces the movement of an interface between the single-phase primary solid solution and the neighboring two-phase region in a diffusion couple as a function of time. The method assumes that $\bar{D}$ is independent of composition. The values obtained agree very closely with those determined from the Matano-Boltzmann treatment.

$\bar{D}$ values were also measured for diffusion in the high-temperature beryllium-nickel β -phase at 1100°C and 1200°C by the Matano-Boltzmann analysis of gradients involving this phase. The values found for a composition of 8 atomic percent nickel are:

$$\bar{D}_{1100^\circ\text{C}} = 2.69 \times 10^{-6} \text{ cm}^2 \text{ per second}$$

$$\bar{D}_{1200^\circ\text{C}} = 3.80 \times 10^{-6} \text{ cm}^2 \text{ per second}$$

The presence of porosity on the beryllium-rich side of the diffusion couples in both the beryllium-iron and beryllium-nickel systems, coupled with information about the movement of the original bond interfaces as a function of time, lead to the conclusion that the beryllium atoms are diffusing more rapidly than either the iron or nickel atoms. The presence of a Kirkendall effect is thus confirmed

by these observations. The movement of the bond interface in the beryllium-nickel diffusion couples is large enough so that values of the intrinsic diffusion coefficients, D_{Be} and D_{Ni} could be obtained. Their variation with temperature may be represented by the relations:

$$D_{Be} = 2.1 \exp [-44 \times 10^3 / RT]$$

$$D_{Ni} = 0.1 \exp [-50 \times 10^3 / RT]$$

The values of the density (ρ) were required as a function of the weight fraction of alloying elements, X , for both alloy systems in order to evaluate the concentration gradients. The values fit very closely to the curves for the mixtures of beryllium and iron atoms and for beryllium and nickel atoms and may be represented by the equations:

$$\rho_{Be-Fe} = \frac{14.53}{7.87 - 6.02X_{Fe}}$$

$$\rho_{Be-Fe} = \frac{16.43}{8.90 - 7.05X_{Ni}}$$

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