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Physical Metallurgy of Uncommon Metals

by

Robert E. Ogilvie

John T. Norton

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Massachusetts Institute of Technology
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Progress Report

Physical Metallurgy of Uncommon Metals

This progress report covers the work carried out during the fiscal year 1960-61 in the Department of Metallurgy at M.I.T. under the supervision of Professors Robert E. Ogilvie and John T. Norton.

The areas of research have been sub-divided into the following categories:

I. Physical Metallurgy

- A. Diffusion of U-Nb Incremental Couples
- B. Radiation Damage in Nickel Crystals
- C. Texture Studies of Cold Rolled Tantalum
- D. Thermal Gradient Effects in U-Mo Alloys

II. Magnetic Research

- A. Magnetic Properties of the $\text{UFe}_2\text{-UMn}_2$ System
- B. Remanent Magnetization of Hematite

III. Crystal Chemistry

- A. Theoretical Studies in Crystal Chemistry
- B. Factors Controlling Formation of C11, C40 and C54

Type Structures

At this time a brief summary of these particular projects is given. Some have been completed while the others are well underway.

I. Physical Metallurgy

A. Diffusion of U-Nb Incremental Couples

Incremental couples at 10% intervals across the U-Nb binary have been prepared and diffused at temperature from 800°C, at the uranium rich end, to 1700°C at the niobium end of the binary. Of the forty-one couples that have been prepared, approximately one-quarter have been analyzed with the electron microbeam probe. In every case, both elements are measured simultaneously.

B. Radiation Damage

Irradiation damage of nickel single crystals bombarded with 3 Mev electrons from a Van de Graaff generator has been studied by Kossel line techniques. Changes of lattice parameter and x-ray line breadth were determined for crystals bombarded with integrated dosages of 10^{16} , 10^{17} , and 10^{18} electrons/cm² at liquid nitrogen temperature. It is concluded from analysis of the Kossel patterns that: (1) most defects anneal out below room temperature, (2) remaining defects exist as Frenkel defects associated with impurity atoms or other sinks, (3) all defects are mobile and anneal out below 400°C. Subsequent annealing studies support this conclusion. The sources of errors in lattice parameter determination and their corrections have been quantitatively treated. Using an electron microbeam probe to obtain the Kossel patterns, the relative precision of the lattice parameter obtained is in some cases better than 1 part per 300,000.

C. Texture Studies of Cold Rolled Tantalum

The cold rolled texture of tantalum is described by the (200) and (110) pole figures presented in Figures 1 and 2. This texture may be approximated by the ideal orientations, $\{112\} \langle 011 \rangle$, $\{100\} \langle 011 \rangle$, and $\{111\} \langle 112 \rangle$. The first predominates with the second strong and the third diffuse. However, the set of orientations $\{111\} \langle \text{arbitrary} \rangle$ appears somewhat stronger than the set $\{100\} \leftrightarrow \{112\} \langle 011 \rangle$. The slight increase in (200) pole density near the rolling and transverse directions possibly indicates a very weak $\{100\} \langle 001 \rangle$ orientation.

These results are generally in agreement with those of Pugh and Hibbard⁽¹⁾ although they found the $\{112\} \langle 011 \rangle$ orientation to be much stronger than the others. However, pole figures obtained by Muller⁽²⁾ indicate that the $\{100\} \langle 011 \rangle$ orientation is the strongest.

The rolled texture for tantalum is similar to those of other body centered cubic metals such as iron, molybdenum and niobium. It differs in having a well defined $\{112\} \langle 011 \rangle$ which in at least two investigations has been found to be the strongest single orientation. In the more common bcc textures the major orientation is the $\{100\} \langle 011 \rangle$ and the $\{112\} \langle 011 \rangle$ is diffuse.

Pugh⁽¹⁾ has attributed the strength of the $\{112\} \langle 011 \rangle$ to a preference for the (110) over the (112) as a glide plane in tantalum. Bakish⁽³⁾ has reported preliminary investigations at room temperature indicating glide on the (110) and (112) planes with the former preferred.

Mechanical Properties. The directionality of Young's modulus, yield strength (.01% offset) and tensile strength is presented in Table I.

Fracture tended to occur parallel to either the rolling or transverse directions and was brittle in appearance. Fractures parallel to the transverse direction were accompanied by 2% to 5% elongation; those parallel to the rolling direction by no measureable elongation. Responsibility for this type of fracture may be attributed to voids aligned by rolling principally in the rolling direction.

On this basis, barring other factors, one would expect the tensile strength to be a minimum at intermediate angles because the maximum shear stress is then aligned in these weak directions. This is not the case, perhaps indicating that the tensile strength should be greater at these angles for crystallographic reasons.

Young's modulus exhibits maxima in the transverse and rolling directions and a minimum at about 35° from the rolling direction. Assuming that the reciprocal of the measured Young's modulus ($1/E$) is the sum of the weighted $1/E$ of all crystals in the sheet and that all crystal orientations present may be approximated by a few ideal orientations and utilizing compressibility data obtained by Bridgeman⁽⁴⁾ approximate values of the compliances " S_{ij} " are calculated. In Table II the stiffness constants " c_{ij} ", obtained from these " s_{ij} ", are compared to those determined by Bolef⁽⁵⁾ using a high frequency resonance technique. The agreement is good considering the approximations involved in these calculations.

Shear anisotropy constants, $A = 2c_{44}/c_{11} - c_{12}$, for tantalum and several cubic metals are given in Table III⁽⁵⁾. The values of "A" for the six bcc transition elements excluding Fe are considerably different from those of the other metals.

References

1. J. W. Pugh and W. R. Hibbard: Trans. ASM, 48, 526 (1956)
2. H. Muller; Zeitschrift fur Metall kunde, 49, 575 (1958)
3. R. Bakish; Acta Met, 6, 120 (1958)
4. P. W. Bridgeman, Proc. Amer. Ac. Acts and Sc., 77 187 (1949)
5. D. I. Bolef; Journ. Appl. Phys. 32, 100 (1961)

Table I

Average values of mechanical properties

Angle from Rolling Direction	Young's Modulus x10 ⁻⁶ psi	Ultimate Tensile Strength x 10 ⁻³ psi	0.01% Offset Yield Strength x 10 ⁻³ psi
0	26.9 [±] 0.2	106 [±] 22	46.3 [±] 1.3
15	26.3 [±] 0.5	127 [±] --	43.7 [±] --
30	25.9 [±] 0.3	120 [±] 0	52.0 [±] 0.9
45	26.1 [±] 0.1	119 [±] 0.5	51.1 [±] 4.4
60	26.6 [±] 0.0	125 [±] --	45.8 [±] 1.0
75	27.7 [±] 0.7	112 [±] --	43.1 [±] --
90	28.7 [±] --	97 [±] --	56.5 [±] --

Table II

Investigator	Units of 10^{11} dyne/cm ²			Units of 10^{-13} cm ² /dyne		
	C ₁₁	C ₁₂	C ₄₄	S ₁₁	S ₁₂	S ₄₄
Ganow	27.6	16.2	7.65	6.39	-2.36	13.06
Bolef	26.7	16.1	8.25			

Table III

Shear anisotropies "A" for cubic elements

fcc	A	bcc	A
Cu	3.2	Li	9.4
Ag	2.9	Na	8.1
Au	2.7	K	6.3
Ni	2.6	V	0.79
Pd	2.4	Nb	0.51
Al	1.2	Ta	1.6
Pb	3.9	Cr	0.86
Th	3.6	Mo	0.76
		W	1.0
		Fe	2.4

FIGURE 1 - (200) POLE FIGURE FOR COLD ROLLED TANTALUM REDUCED 92.5% IN THICKNESS. IDEAL ORIENTATIONS:

- {112} <110> ▽ {111} <112>
 □ {001} <110>

FIGURE 2 - (110) POLE FIGURE FOR COLD ROLLED TANTALUM REDUCED 92.5% IN THICKNESS. IDEAL ORIENTATIONS:

○	{112} <110>	▽	{111} <112>
□	{001} <110>		

D. Thermal Gradient Effects on Uranium - 10% w/o Molybdenum Alloys

This work has as its general objective the evaluation of the effects of a thermal gradient on a Uranium-10% w/o molybdenum alloy. This fuel alloy will be used in the Enrico Fermi Fast Breeder Reactor and is being considered for other reactors. A U-10% w/o Mo alloy contains enough Mo to stabilize the isotropic gamma phase at room temperatures. However, previous work on its transformation kinetics indicate that when at elevated temperatures for sufficient time, the gamma phase transforms to the undesirable, anisotropic alpha plus delta phases. These are undesirable for use in a reactor because of dimensional instability.

The experiments conducted imposed on this alloy temperature gradients comparative to those in an operating reactor. The purpose was to find what the effects of such gradients would be on the transformation kinetics of the alloy, and on the movements of molybdenum and carbon within the alloy.

These effects were measured by means of x-ray diffraction, micro-hardness, metallographic inspection, electron microbeam probe analysis, and chemical analysis. It was found by these methods that the transformation zone (from gamma to alpha plus delta) begins in the alloy at a time sooner than two hours and continues to grow in size for the longer time runs. There was no significant carbon or molybdenum diffusion detected.

On this basis the Fermi Reactor fuel pins will transform after a relatively short period of operation. However the effects of radiation on this transformation are not yet thoroughly understood. Earlier work indicates radiation may act to retard or inhibit transformation. It is recommended that further experimental work be conducted at longer times, and if possible at steeper gradients, to determine whether or not carbon and molybdenum diffusion can be detected. The next logical step would be to repeat this work in a radiation field to determine its effect.

II. Magnetic Research

A. Magnetic Properties of the $\text{UFe}_2\text{-UMn}_2$ System

Considerable difficulty has been encountered in making high purity U-Fe-Mn alloys and a new series is being prepared. The alloy U(Fe,Mn) was found to be paramagnetic from 480°K to 10°K .

B. Remanent Magnetization of Hematite

In the last progress report we presented some new magnetic phenomena of hematite single crystal, which led to a much better understanding of the controversial problems of this material. This past year we have devoted considerable work to the magnetic behavior in the transition region.

Experimental Results and Discussion

1. The remanent magnetization along particular directions in the (111) plane and along the $[111]$ direction of a rectangular prism of hematite single crystal has been measured during a complete cycle of temperature change between 488°K and 77°K . These results are illustrated in Figure 1. Curve 2 shows the existence of the ferromagnetism below the transition and curves 1 and 2 show the complimentary character which indicates that the ferromagnetism in the (111) plane above the transition and along the $[111]$ direction below transition are of the same nature. This important observation is not in agreement with Néels argument that the weak ferromagnetism is due to Fe_3O_4 impurities and it is not consistent with Li's, and Jacobs and Bean's theory of unbalanced antiferromagnetic domain walls.

2. A small spherical sample of natural hematite has been used to measure the remanent-temperature relationship and the thermal hysteresis effect for each of three mutually perpendicular directions of the crystal in the temperature range under consideration. In Figure 2, curves 1 and 2 show the remanence along two mutually perpendicular directions in the (111) plane and curve 3 along the $[111]$ direction. Since the sample used has never been disturbed by any magnetic field higher than a few oersteds, the χ -T curves should represent the true remanence-temperature relationship of the three mutually perpendicular directions of the sample. These curves are very similar to the spontaneous magnetization-temperature and σ_0 -T curves reported in the last progress report and similar to the curves in Figure 1 of this report, except that the magnitude is smaller. This similarity indicates that the method for obtaining the spontaneous magnetization and the susceptibility curves have been done in a proper manner and hence the conclusions drawn from them are correct. These three loops together give the representation of the weak ferromagnetic state in the ascending and descending temperature between 488° and 77°K . A two-dimensional graphical representation of the ferromagnetic state has been made. This was done as follows: The resultant curve for the basal plane was obtained by combining the corresponding branch of curves 1 and 2. From this resultant curve, and curve 3, the direction and magnitude of the remanent magnetization vector at each temperature was calculated and the results were plotted in Figure 3.

The most interesting feature is that when the temperature decreases through the transition region the remanent magnetization vector turns from the basal plane toward the $[111]$ direction, and, at the same time it diminishes in magnitude. While the temperature increases through transition region the vector turns back from the $[111]$ direction toward the basal plane, and, at the same time, its magnitude increases. Thus turning seems to be continuous through a temperature range of about 140°K . This leads to the conclusion that the mean direction of the antiferromagnetic spin of each sublattice would turn continuously between the $[111]$ direction and the basal plane as the temperature changes through the transition region.

3. Another experiment has been carried out as follows: The spherical sample was rotated in the field gradient, and the remanent magnetization was measured along different directions in the plane containing the $[111]$ direction and the direction of the remanent magnetization in the (111) plane. Figure 4 shows that the polar plot of the measured magnetization vs angle of observation gave a circle passing through the origin. The direction of the center point of this circle was the direction of magnetization, and the diameter of the circle was the magnitude of magnetization. The three magnetization vectors, at three different temperatures determined this way, fitted in Figure 2 very well. For the sake of completeness the three vectors are shown in Figure 2. This experiment confirms the remanent magnetization-temperature relationship in the transition region by a direct magnetic measurement.

FIG 1. VARIATION OF REMANENT MAGNETIZATION WITH TEMPERATURE AND HYSTERESIS EFFECT OF NATURAL HEMATITE SINGLE CRYSTAL (RECTANGULAR PRISM)
 (1) ALONG A CERTAIN DIRECTION IN THE (111) PLANE
 (2) ALONG $[111]$ DIRECTION.

FIG.2. VARIATION OF REMANENT MAGNETIZATION WITH TEMPERATURE AND HYSTERESIS EFFECT OF NATURAL HEMATITE SINGLE CRYSTAL (SPHERE C)
 (1) ALONG A DIRECTION X NEAR THE DIRECTION OF REMANENT MAGNETIZATION IN THE (111) PLANE
 (2) ALONG A DIRECTION Y IN THE (111) PLANE AND PERPENDICULAR TO X
 (3) ALONG $[111]$ DIRECTION

FIG. 3 PROJECTION OF REMANENT MAGNETIZATION IN (111) PLANE
RELATION AMONG REMANENT MAGNETIZATION, CRYSTALLOGRAPHIC AXIS, AND TEMPERATURE PLOTTED IN POLAR COORDINATE IN THE TRANSITION REGION OF NATURAL HEMATITE SINGLE CRYSTAL (SPHERE C)

FIG. 4. REMANENT MAGNETIZATION PLOT IN POLAR COORDINATE AT THREE DIFFERENT TEMPERATURES IN THE TRANSITION REGION OF NATURAL HEMATITE SINGLE CRYSTAL (SPHERE C)

III. Crystal Chemistry

A. Theoretical Studies in Crystal Chemistry

The concept of space filling proves to be an excellent method for presenting geometrical relationships of different crystal structures. Space filling ϕ is defined as the quotient volume of the atoms in a unit cell over volume of the unit cell. By making certain assumptions concerning which of the supposedly rigid and spherical atoms are touching each other one may express the volume of the unit cell in terms of the radii of the involved atoms. The calculation is most easily demonstrated on the case of CsCl with Cs as A and Cl as B partners

$$\phi = \frac{4/3 \cdot \pi (r_{\text{Cs}}^3 + r_{\text{Cl}}^3)}{a^3} \quad (1)$$

where a denotes the unit cell constant

B-B contact: Only the Cl ions are touching each other

With $a = 2r_{\text{Cl}}$ and $\xi = \frac{r_{\text{Cs}}}{r_{\text{Cl}}}$ follows

$$\phi_{\text{Cl-Cl}} = \frac{\pi}{6} (\xi^3 + 1) \quad (2)$$

A-B contact: Cs ions and Cl ions are in contact only

Here $\frac{a\sqrt{3}}{2} = r_{\text{Cs}} + r_{\text{Cl}}$ hence

$$\phi_{\text{Cs-Cl}} = \frac{\sqrt{3}}{2} \frac{\xi^3 + 1}{(\xi + 1)^3} \quad (3)$$

A-A contact: Cs ions are in contact only with other Cs ions

Here $a = 2r_{\text{Cs}}$ and thus

$$\phi_{\text{Cs-Cs}} = \frac{\pi}{6} \frac{\xi^3 + 1}{\xi^3} \quad (4)$$

The space filling of the CsCl structure depends therefore on the radius ratio ξ . The three branches can be studied in Fig. 1a in a $\log \phi - \log \xi$ diagram. The following correlations between the kind of structure and the shape of the space filling curve exist:

1. Space filling values of different structure types with the same composition differ only by a factor independent of ξ . See Fig. 1a and 2.

2. Structures with commutative partial structures have a symmetrical space filling curve with a symmetry line at $\xi = 1$. For example CsCl, NaCl, ZnS, NaTl in Fig. 1a.

3. Homeotect structures have identical space filling curves. For example wurtzite and sphalerite in Fig. 1 and the three Laves phases in Fig. 2.

4. Two structures standing in the relationship of type and anti-type to each other have space filling curves which are related to each other like image and minor image. For example CaF_2 and Mg_2Si in Fig. 2

5. Two structures which have identical partial structures can be recognized in the space filling diagram, as they assume the same space filling value at $\xi = 0$ and $\xi = \infty$. For example MgCu_2 and SiO_2 in Fig. 2.

6. The positions of the discontinuity point on the space filling curve can be related to Laves construction formula.

Space filling diagrams can be used in three different ways. Due to different settings of axes and shift or origin virtually identical structures have in the past not always been recognized as identical. The space filling is independent of setting of axes and shift of origin. The curves of identical structures have to coincide. This is demonstrated for the pairs SnS-GeS and CrB-CaSi in Fig. 3. Slight deviations are due to slightly different free parameters. Space filling values can be further used to predict possible pressure structures. The third application of the space filling diagram makes use of the position of the discontinuity points. Based on the assumption that in ionic structures ions of the same charge should never touch each other, Goldschmidt developed semi-empirical stability laws for valence compounds. The space filling curve provides a graphical representation of these geometrical structure arguments. The discontinuity points of the space filling curve prove to be stability boundaries. A structure energy calculation shows that these boundaries determined by space filling curves have actual meaning. This can be seen by comparing Fig. 1a with 1b. The space filling diagram can be useful also in the case of semi-ionic compounds. Fig. 3 shows the space filling curves of monosilicide and boride structures. The predicted stability ranges check well with the observed ranges.

This study will be published in Z. Krist. and it is advised to refer to this paper for detailed information.

Experimental Studies

The Structure of (Re, Ti)Si₂

In the course of a general study of the conditions for the formation of disilicides the pseudo-binary systems ReTi₂-TiSi₂ was investigated. The structures of ReSi₂ and TiSi₂ are related. Both of them show hexagonal silicon nets which are centered with metal atoms but with different stacking of these nets. The stacking sequence of the nets in the ReSi₂ structure is of the AB type, that of TiSi₂ of the ABCD type. It was of interest to establish whether an intermediate phase existed and whether its structure would be of the stacking type ABC. It was found that a compound (Re,Ti)Si₂ occurs and that it crystallizes with a hexagonal unit cell with the approximate lattice constants

$$a = 4.6 \text{ \AA} \quad \text{and} \quad c = 6.5 \text{ \AA}$$

The intensities of the diffraction lines seem to correspond to those of the expected C40 crystal structure type. An intensity calculation will now be undertaken to prove the structure proposal.

$$U_{AB} \frac{n}{(n-1)} (r_A - r_B)$$

FIG. 1a SPACE FILLING IN DEPENDENCE OF ε

FIG. 1b STRUCTURE ENERGY IN DEPENDENCE OF ε

FIG. 2 SPACE FILLING OF 4 AB₂ STRUCTURES
AND ONE ANTITYPE STRUCTURE

(TiO₂ with $\frac{c}{a} = \frac{\sqrt{2}}{1+\sqrt{2}}$, SiO₂ as β cristobalite)

FIG. 3 SPACE FILLING OF DIFFERENT AB STRUCTURES