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High-pressure X-ray diffraction studies of Cm–Bk alloys: contribution to the actinide pressure-phase diagram[1]

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Abstract

Curium–berkelium alloys were studied by X-ray diffraction up to 53 GPa to probe their structural behavior under pressure. Two different alloy compositions were studied successfully in this work: one was a $Cm_{0.70}$–$Bk_{0.30}$ alloy and the second was a $Cm_{0.46}$–$Bk_{0.54}$ alloy. The goal was to understand the phase and relative volume behavior of both alloys in terms of: (1) bonding, (2) the elements' electronic configurations and (3) their pressure behavior relative to that reported for the pure Am–Cf metals. Given here are the results of the high-pressure studies of these Cm–Bk alloys, and a discussion of the significance of the findings with respect to the published actinide pressure-phase diagram.

Keywords: Cm; Bk; Alloys; Pressure; X-Ray study

1. Introduction

Considerable progress has been made in the last two decades in studying transplutonium metals under pressure using X-ray diffraction techniques. This has been due largely to the improvement of diamond anvil pressure cells (DACs), detector systems and the availability of larger quantities of these elements. Studies of the lighter actinide metals, especially U and Pu, have been driven by special (e.g., reactor and weapons) interests in these metals, and have employed experimental techniques besides DAC technology.

Important advances with f-element metals have been accomplished by employing synchrotron radiation for DAC studies, which offers experimental advantages especially in the megabar pressure region. In this regard, the unique behavior of Th up to 300 Mbar [1] and the detailed behavior of Ce under pressure [2] have utilized synchrotron radiation. Investigations of the transplutonium metals have had to rely on conventional X-ray generators for performing pressure studies on actinide metals through Es. Studies of the transplutonium metals have only been reported up to pressures of ~60 GPa, although there is a need for attaining even higher pressures to understand fully their pressure behavior.

One of the earlier findings [3] for these transplutonium metals was that Am formed a structure between 15–18 GPa that was assigned as an α-uranium type structure. Formation of this structure indicated that the 5f-electrons of Am were forced to participate in the metallic bonding, as do those of uranium at normal pressures. It is now generally accepted that Am exhibits four structural phases (Am I, II, III and IV) below 60 GPa, with the fourth being the α-uranium, orthorhombic phase [4–6]. Subsequent studies with Cm, Bk and Cf lead to the observance of similar high-pressure structures, and the conclusion that their 5f-electrons eventually became involved in bonding as a result of applying pressure [4–6]. Recent attempts to extend high-pressure studies to the next higher actinide, Es, have met with only limited success [7], due to the extreme radiation effects encountered with the most available isotope of the element. The reader is referred to reviews concerning the detailed pressure behavior of these f elements [4–6].

Studies of transplutonium alloys were initiated to compare in greater detail the structural changes occurring

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between neighboring elements under pressure. The first transplutonium alloys examined were Bk–Cf alloys (generated by the beta decay of Bk-249 metal), which were followed by studies of Am–Cm alloys [4–6]. We report here structural studies of two Cm–Bk alloys, nominally 46 and 70 atom % Cm, under pressure up to 53 GPa, and the significance of their behavior for the transplutonium pressure-phase diagram.

2. Experimental

2.1. Materials

The Cm-248 (containing 3 atom % Cm-246) and Bk-249 isotopes were made available through the US Department of Energy's program for producing transplutonium isotopes for research. The purified isotopes were received as chloride salts and purified further by a cation exchange process using hydrochloric acid [8].

The alloys were obtained by the procedure described previously for the preparation of pure Cm and Bk metals [9]. For preparation of the Cm–Bk alloys, the desired quantities of the two elements (for 25, 50 and 75 atom % Bk) were combined as a chloride solution and the mixed trifluorides precipitated by adding HF. After drying, these fluoride salts were treated (three separate times) under 1200 mm of fluorine at 400°C to remove traces of oxygen and water. The resulting anhydrous, mixed fluorides of each composition were then individually reduced with lithium metal under vacuum ($<10^{-7}$ torr) using a programmed temperature up to 1100°C. The products were obtained as bright metallic spheroids in tungsten holders.

2.2. High-pressure experiments

The energy dispersive X-ray diffraction studies of the alloys were performed at room temperature using a Syassen–Holzapfel diamond anvil pressure cell, modified and constructed at the European Transuranium Research Institute. The energy dispersive instrumentation used is located at Oak Ridge National Laboratory. The procedure was as described previously [10], with the exception that a rotating tungsten anode was used in place of a conventional tungsten X-ray tube in the X-ray generator. The rotating anode generator provided a fourfold increase in intensity, which allowed good diffraction spectra to be obtained in shorter times.

A portion of each Cm–Bk alloy was loaded together with ruby chips in a 200 micron diameter hole in an Inconel gasket mounted on one of the two diamond anvils. Silicone oil (Dow-Corning D-205; predried with molecular sieves) was used as the pressure transmitting medium. The ruby chips, in intimate contact with the sample, permitted the determination of the applied pressure via the shift of the ruby fluorescence [11], following excitation by an argon laser.

In the high-pressure measurements, two Bragg angles (nominally, 5 and 7 degrees) were defined by a double conical slit assembly. The exact angles were measured using UC as a standard in the exact configuration used for analyzing the alloy samples. Lattice spacings were calculated as a function of the applied pressure. After assigning indices to the data, the cell volume of the alloy was calculated for each pressure. The relative volumes were calculated using the latter volumes and the initial volume of the double hexagonal close packed (dhcp) form of the alloy at atmospheric pressure. The ENDIX program was used for calculating theoretical spacings [12] and a modified POWLES program employed for the least squares calculations of the lattice parameters [13].

3. Results and discussion

3.1. Cm–Bk alloys under pressure

The goal of the investigation was to examine the Cm–Bk region of the pressure-phase diagram in more detail (e.g., as a function of a ''fractional'' change in atomic number) by studying Cm–Bk alloys. The intent was to prepare and study three different Cm–Bk alloy compositions (25, 50 and 75 atom % Bk). However, during the preparation of these alloys, it was found that the higher vapor pressure of Bk metal, as compared to Cm metal, [14] resulted in a preferential loss of Bk. As a result, the compositions were altered during the preparations and yielded alloys with a higher Cm content. Only two of the three nominal alloy compositions sought were obtained: one with 30 and the other with 54 atom % Bk. The final composition of each alloy was determined based on fluorescence ratios, alpha/beta counting data and considering the lattice parameters of the alloys at atmospheric pressure.

The structural behavior of these two Cm–Bk compositions were monitored by X-ray diffraction up to 53 GPa. With the $Cm_{0.70}$–$Bk_{0.30}$ alloy, two structural transformations were noted. The first was the transformation of the atmospheric pressure, double hexagonal close packed (dhcp) phase to a face centered cubic (fcc) type structure, which occurred at 12 GPa. This fcc structure then changed to a third phase at 35 GPa, which was retained up to the maximum pressure studied, 53 GPa. This third phase will be addressed in a later section.

The second alloy studied under pressure was the $Cm_{0.54}$–$Bk_{0.46}$ alloy. The starting structure for this alloy was also dhcp, and it converted to the fcc-type structure at 8 GPa. The fcc structure then converted to a third structure at 24 GPa, which was retained up to 53 GPa. It was comparable to the third structure seen in the first alloy and will also be discussed later.

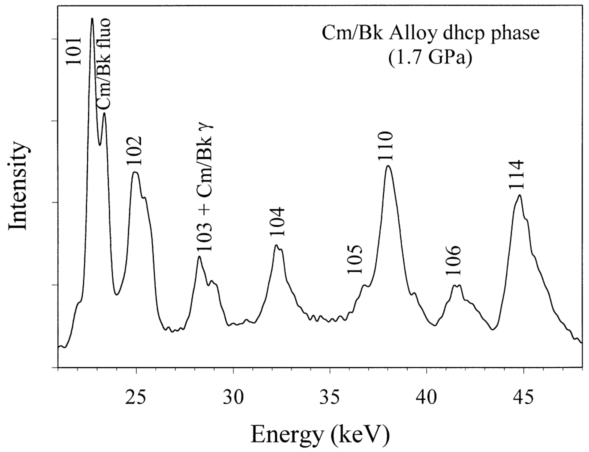

Fig. 1. Energy dispersive X-ray spectrum at 5 degrees for the dhcp form of the 70% Cm–30% Bk (atom %) alloy at 1.7 GPa. Peaks are identified as diffraction (indices), and fluorescence or gamma emissions.

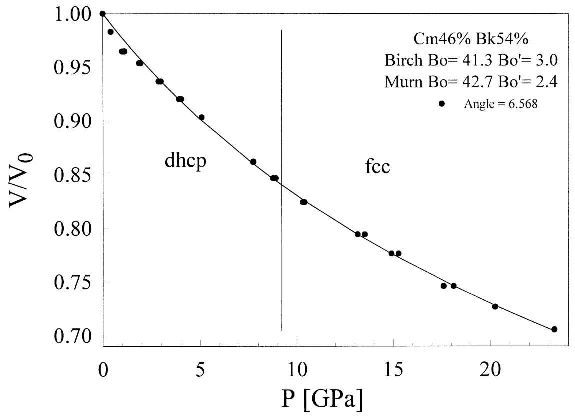

Fig. 3. Compression curve for the 46% Cm–54% Bk (atom %) alloys up to 23 GPa, showing the smooth, relative volume–pressure relationship through the dhcp–fcc phase transition for the 6.568 degree diffraction angle employed.

Both of the Cm–Bk alloys underwent a smooth conversion from dhcp to fcc under the application of pressure, without any indication of a sharp change in relative volume across the phase boundary. X-Ray data for the dhcp (at 1.7 GPa) and for the fcc (at 19 GPa) structures observed with the $Cm_{0.70}$–$Bk_{0.30}$ alloy are shown in Figs. 1 and 2. Comparable data and pressure behavior were obtained with the second alloy sample. The diffraction peaks in the two figures are labeled with the assigned indices; the actinide gamma and fluorescence peaks are also identified. The compression curve for the $Cm_{0.46}$–$Bk_{0.54}$ alloy up to 23 GPa obtained at the 6.568 degree diffraction angle is shown in Fig. 3. Using the compression data from both alloys, and the Birch [15] and Murnaghan [16] equations of state, we calculated a bulk modulus of 41.3 GPa and a B'_o of 3.0 (Birch equation), and a bulk modulus of 42.7 GPa and a B'_o of 2.4 (Murnaghan equation). Similar modulii were calculated for the other Cm–Bk alloy. These modulii are in line with those reported for the pure Am–Cf metals, which range from 23 to 45 GPa (Cm, 33(5) GPa; Bk, 25(5) GPa), but are much lower than the modulii of the Th–Pu metals [3]. These lighter actinide metals are far less compressible, as they have itinerant f-electrons and exhibit a higher metallic valency, than the transplutonium metals at these lower pressures.

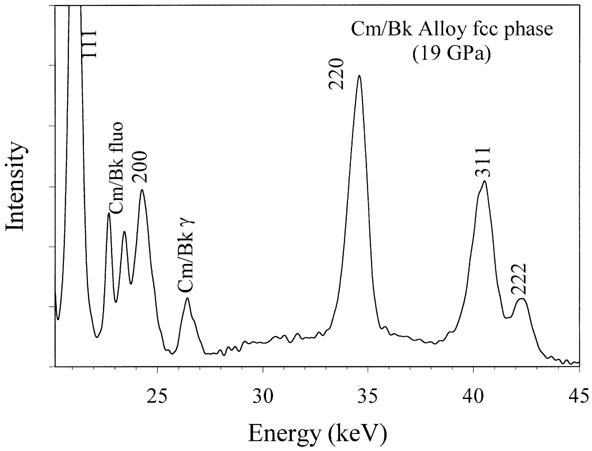

Fig. 2. Energy dispersive X-ray spectrum at 5 degrees for the second high-pressure phase (fcc) for the 70% Cm–30% Bk (atom %) alloy at 19 GPa. Peaks are identified as diffraction (indices), and fluorescence or gamma emissions.

3.2. The actinide metal pressure-phase diagram and the third phase of the Cm–Bk alloys

Studies of the first four transplutonium metals under pressure performed by several researchers have been summarized [4–6]. These trivalent metals undergo two or three structural transitions under pressure and reportedly form an α-uranium structure at the higher pressures, as a result of their f-electrons becoming delocalized. The pressure sequence (dhcp, fcc, fcc′ (a distorted phase), orthorhombic) is similar to that exhibited by some of the trivalent lanthanide metals [5]. There has been some disagreement about the exact nature of this third phase (identified fcc′); a triple-hexagonal close packed structure (hexagonal/6) has also been proposed for it [17]. In addition, theory suggests that the actinides may again form symmetrical structures at even higher pressures (e.g., for uranium, the α-uranium structure may become bct, and then bcc) [18]. Thus, the structures for these higher pressure phases may become more difficult to define, while high-quality, experimental structural data may become more difficult to obtain.

Of the first four transplutonium elements studied under pressure, Cm represents a special case. It is the most resistant of these metals to delocalization of its 5f-electrons by the application of pressure; this result is in part due to its stable, trivalent-metal configuration ([Rn core]$4f^75d^17s^2$) [19]. The intent of this work was to examine in closer detail the structural changes occurring in this region of the series by studying the pressure behavior of Cm–Bk alloys, and referring to the established pressure behavior of selected lanthanide metals.

It is important to note with regard to lanthanide behavior, that Sm is the highest member where pressure appears to induce delocalization of the 4f-electrons (e.g., reflected by the formation of a bct structure) [5,6,20]. With Gd, the next trivalent lanthanide metal and electronic homolog of curium, the high pressure phase retained up to 106 GPa is reported to be trigonal (''distorted fcc''-like), which does not suggest the presence of delocalized f-electrons [5,6,21]. Given the greater spatial extension of the 5f-electrons, it is expected that they may delocalized at lower pressures than the 4f-electrons (e.g., delocalization is observed with Am below 25 GPa [4]).

In our studies of the two Cm–Bk alloys, the first structural change (dhcp to fcc), and the associated transformation pressures, were in reasonable accord with those expected, based on interpolation of reported Am, Cm and Bk data [4–6]. A graphical projection of these transformations for Am, Cm, Bk, plus the Am–Cm and Cm–Bk alloys, is shown in Fig. 4. The resistance of Cm to the structural transformation under pressure, and the apparent influence of Cm on the transformation pressures for the five alloys, can be seen in Fig. 4.

We were unable to assign satisfactorily the structure of the third phase formed between 35 and 53 GPa by both of the Cm–Bk alloys. This in part arose from the greater complexity and the broadening of the diffraction peaks at the higher pressures. Based on general considerations, the two most probable phases would likely be the α-uranium or the ''distorted fcc'' structures. However, in previous studies [4–6] with pure Cm and Bk, a ''distorted fcc'' structure was not observed as one of the pressure phases. Additional experimental results will be necessary to resolve fully this issue and identify the structure-type, which will provide important insights into this portion of the actinide pressure-phase diagram. We plan to perform additional high pressure investigations on both Cm–Bk alloys and pure Cm, hopefully to even higher pressures than achieved in these initial studies. The findings will be presented at a later time.

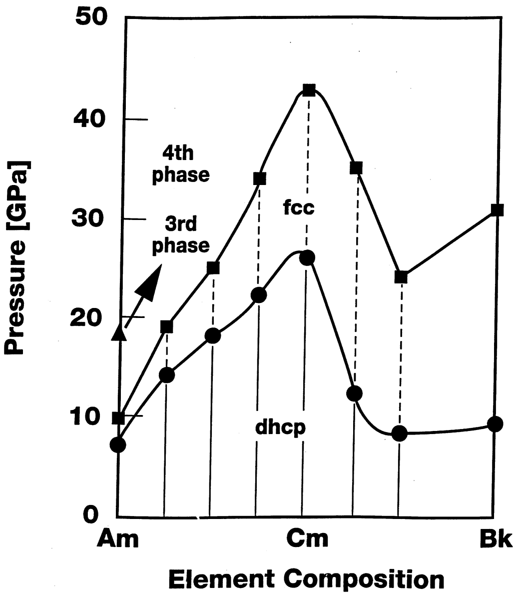

Fig. 4. Pressures for the dhcp to fcc, and the fcc to third phase, transitions for the Am to Bk metals, and the Am–Cm and the Cm–Bk alloys. Plot reflects the resistance of pure Cm and Cm-containing alloys to phase changes with applied pressure.

4. Summarizing comments

The high-pressure studies performed on the two Cm–Bk alloys containing 70 and 54 atom % Cm, confirmed that higher transition pressures tend to be encountered with Cm bearing, near-neighbor alloys. The Cm-rich alloy had transition pressures higher than those for comparable transitions in pure Am and Bk, while the 54 atom % Cm alloy was affected less. The structural nature of the third phase observed between 35–53 GPa with both of the Cm–Bk alloys has not been resolved. Additional experimental studies are planned to address the structure of this phase, which will have important ramifications for understanding and advancing the actinide pressure-phase diagram.

Acknowledgements

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