Journal of Alloys and Compounds, 213/214 (1994) 363–365
JALCOM 4092

Twinning as a clue to a CDW-like behavior and to a lack of SME in plutonium metal

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Abstract

The twinning systems of alpha phase Pu metal have been reported by Zocco *et al.* (*Proc. XII Int. Congr. for Electron Micros.*, 1990, p. 1014). Twinning modes and charge-density wave (CDW) states have both been reported for the CDW materials $2HTaSe_2$ and TiNi alloys. The latter alloys also show shape memory effect (SME). The similarities in properties of α-Pu and TiNi alloys have recently been pointed out by Sandenaw (*J. Nucl. Mater., 189* (1992) 343). A possible clue to a CDW-like behavior and a lack of SME in α-Pu may be in the twinning systems observed. Microtwinning has been suggested as interfering with flow of itinerant electrons and thus causing a rise in electrical resistivity as reported for the TiNi alloys (Wang *et al., J. Appl. Phys., 43* (1972) 97). The latter workers report a one-to-one correspondence between mechanical "memory" effect and electrical resistivity. α-U exists with many twinning modes (Frank, *Acta Metall., 1* (1953) 71) but does not show any CDW behavior except at low temperatures. Therefore, twinning alone cannot be the source of a CDW-like behavior in α-Pu metal. Bak (*Rep. Prog. Phys., 45* (1982) 587) explained that the conduction electron density in a distorted phase is spacially modulated to form the CDW which accompanies the periodic lattice distortion (PLD). There appear to be competing periodicities (a PLD) in the complex α-Pu structure because the eight crystallographically different Pu atoms of the unit cell are seen to occur in a different but reproducible pattern in each of three directions on the *a-c* plane of the distorted pseudo hexagonal structure (Smith *et al., ACS Symp. Series, No. 216, Plutonium Chemistry* (1983) Fig. 1). It is suggested that the modulation of the conduction electrons, in three competing periodicities (chains) of the α-Pu lattice, should result in three different competing CDW-like states. The interference between three different CDW-like states may lead to the inability to see any one CDW-like state in α-Pu by neutron diffraction. The α-Pu structure is more complex than those of the CDW materials $2HTaSe_2$ and TiNi alloys which also show twinning and a hexagonal structure. The twinning planes and twinning (shear) directions of single-crystal TiNi have been described with only the number one and zeros. (Miyazaki and Wayman, *Acta Metal., 36* (1988) 181). The twinning planes and twinning directions of α-Pu were described by Zocco *et al.* with the numbers 1, 2, 3, 5 and 7 (and zeros). The greater complexity of twinning systems in α-Pu metal may explain an inability to see CDW states by TEM. This complexity could explain the lack of SME in Pu metal.

1. Introduction

The physical property behavior of plutonium (Pu) metal is in general like that shown by incommensurate crystals, *i.e.* there is a thermal hysteresis, a time dependence, a sample dependence, and a dependence on the thermal history of the sample. Arguments have been presented for the possibility of incommensurate and commensurate charge-density wave (CDW) states in alpha-phase plutonium (α-Pu) [1]. A CDW has been described as a coupled distortion of the conduction electron density and the underlying lattice.

Twinning modes and charge-density wave (CDW) states have both been reported for the CDW materials 2HTaSe [2] and TiNi [3]. Alloys of Ti and Ni also show shape memory effect (SME). Experimental evidence suggests that all SME alloys consist of internally twinned martensites.

The similarities in physical properties of α-Pu and TiNi alloys have been recently pointed out by Sandenaw [4]. There should be the possibility of SME in the alpha-phase range of Pu metal because of the presence of twinning modes, as reported by Zocco *et al.* [5].

The electrical resistivity vs. temperature curve for the alpha-phase range of Pu metal [6] also suggests that Pu metal could show SME (Fig. 1). The hysteresis loop in electrical resistivity between 313 K and 428 K is like that shown by Au–49%Cd (an SME alloy) [7].

2. A possible source of a CDW in alpha-phase plutonium

Bak [8] explained that the conduction electron density in a distorted phase is spacially modulated to form a

SSDI 0925-8388(94)04092-I

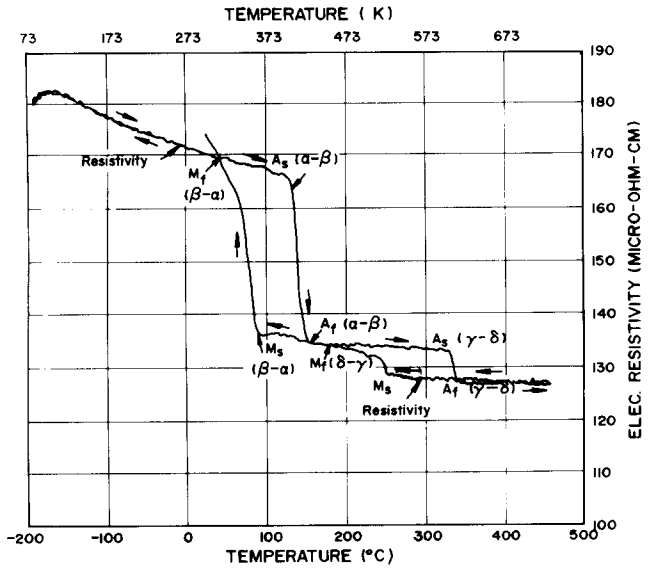

Fig. 1. Electrical resistivity versus temperature for plutonium metal between 73 and 733 K [6].

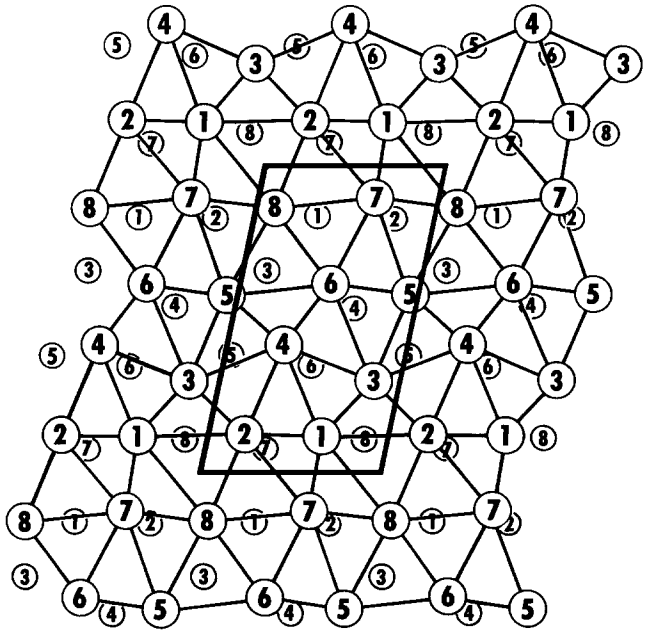

Fig. 2. Crystal structure of α-phase Pu. The large numbered circles represent the arrangement of the eight different types of atom on the a–c plane of the monoclinic structure. The heavy parallelogram represents the unit cell of 16 atoms. (By permission of Smith *et al.* [9]).

CDW which accompanies a periodic lattice distortion (PLD). Alpha-phase Pu appears to qualify as having a complex PLD structure. There appear to be competing periodicities (PLDs) in the complex α-Pu structure because the eight inequivalent Pu atoms of the unit cell are seen to occur in a different but reproducible pattern in each of three directions on the a–c plane of the distorted pseudo-hexagonal structure, as reported by Smith *et al.* [9]. Their suggested arrangement of inequivalent atoms is shown in Fig. 2. This distorted arrangement of Pu atoms, with their influence on conduction electrons, could be giving the physical property response which suggests CDW-like states.

3. Twinning systems of alpha-phase plutonium

The twinning systems of α-Pu have been reported by Zocco *et al.* [5]. Their research revealed the existence of the following twinning modes:

$K_1 = (201)$, $\eta_2 = [702]$, $K_2 = (20\bar{7})$, $\eta_1 = [10\bar{2}]$

and

$K_1 = (205)$, $\eta_2 = [302]$, $K_2 = (\bar{2}03)$, $\eta_1 = [\bar{5}02]$

The twinning systems are quite complex when compared to those of TiNi, and description of the twinning planes and twinning directions of alpha Pu require the numbers 1, 2, 3, 5 and 7 (plus zeros).

4. Microtwinning, electrical resistivity and SME

Wang *et al.* [10] reported a one-to-one correspondence between mechanical memory effect and electrical resistivity in TiNi alloys. Microtwinning was suggested as interfering with the flow of itinerant electrons and causing a rise in electrical resistivity of TiNi alloy to a maximum at the martensitic transformation temperature. There is such a maximum in the electrical resistivity curve of α-Pu at 100 K (Fig. 1) (also suggestive of SME).

It has been noted above that CDWs, microtwinning and SME are observed for the TiNi alloys. This suggests that twinning is also playing a role in the CDW-like behavior of alpha-phase Pu. Twinning modes could be giving the physical property effects of a CDW, *e.g.* an increase in electrical resistivity on cooling, but twinning alone cannot be responsible. Alpha-phase uranium exists with many twinning modes as reported by Frank [11], but only shows CDW states below 40 K [12]. There is no increase in the electrical resistivity of α-U on cooling below room temperature.

5. Plausible answers to a non-observation of either CDW states or SME in α-Pu

Modulation of the conduction electrons in three competing periodicities (chains), on the a–c plane of the pseudo-hexagonal structure of α-Pu (Fig. 2), should result in three different competing CDW-like states; the interference between these may lead to an inability

to detect even one CDW-like state in α-Pu by neutron diffraction.

The chains of inequivalent Pu atoms, indicated for the a–c plane of the α-Pu structure, should show a continuous distortion on cooling below ambient temperature. This could present an interference to conduction electron motion and give the electrical resistivity increase shown by some incommensurate CDW materials. The structure itself may be causing the physical property response suggestive of CDW-like states.

The twinning planes and twinning directions of single-crystal TiNi have been described with only the number one (1) and zeros by Miyazaki and Wayman [3]. In contrast, the twinning planes and twinning directions for α-Pu were described by Zocco *et al.* [5] with the numbers 1, 2, 3, 5 and 7 (and zeros). The greater complexity of twinning systems in α-Pu may explain a lack of SME, although physical properties (discussed above) suggest that SME should be possible.

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