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Antiferromagnetic–ferromagnetic crossover in UO_2–TiO_x multi-phase systems

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Abstract

An antiferromagnetic (AF)–weakly ferromagnetic (WF) crossover has been found for UO_2–TiO_x multi-phase systems, $(1 - y)UO_2 + yTiO_x$ ($y = 0.05$–0.72, $x = 0$, 1.0, 1.5 and 2.0), when these mixtures are heat treated at high temperature in vacuum. From the powder X-ray diffraction and electron-microprobe analyses, their phase assemblies were as follows: for $x = 0$, 1.0 and 1.5, a heterogeneous two-phase mixture of $UO_2 + TiO_x$; for $x = 2.0$, that of $UO_2 + UTi_2O_6$ for $y < 0.67$, showing characteristic microstructures, and for $y > 0.67$ that of $UTi_2O_6 + TiO_2$ (plus residual minor UO_2). Magnetic susceptibility (χ) of the present UO_2 powder was confirmed to exhibit an antiferromagnetic sharp drop at T_N ($= 30.5$ K). In contrast, χ of these multi-phase systems was found to exhibit a sharp upturn at the respective T_N, while their T_N values remained almost constant with varying y. This χ upturn at T_N is most pronounced for $UO_2 +$ Ti-oxide (titania) systems ($x = 1.0$, 1.5 and 2.0) over the wide mixture ratio above $y \sim 0.10$. These observations indicate that an AF–WF crossover is induced for these multi-phase systems, plausibly due to the interfacial magnetic modification of UO_2 in contact with the oxide partners. © 2001 Elsevier Science B.V. All rights reserved.

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The magnetic properties of uranium dioxide (UO_2) with the cubic fluorite structure have been well studied both experimentally and theoretically [1,2]. From those studies, it is clear that UO_2 is an antiferromagnet with a Neel temperature (T_N) of 30.8 ± 0.3 K, and we have extensive knowledge of the nature of this first-order antiferromagnetic (+ magneto-strictive) phase transition and its (antiferromagnetic) magnetic structure. Extensive magnetic studies have also been reported on various UO_2-based solid solution systems, $U_{1-y}Ln_yO_{2-z}$ (Ln^{3+}; trivalent lanthanides) [3,4]. Those studies show that aliovalent-cation (Ln^{3+}) substitutions for the tetravalent uranium (U^{4+}) cause significant weakening of the antiferromagnetic interaction (via the oxide ion (O^{2-})) between the U^{4+} in the host UO_2 lattice, in combination with thereby-induced oxygen non-stoichiometry (either $z > 0$ or < 0) and the partial oxidation of U^{4+} to U^{5+}. The overall effect of such magnetic dilution and disturbance is a rapid decrease of T_N with y, nearly changing the system to a Curie–Weiss-type paramagnet already around 20–30 mol% substitution level ($y = 0.20$–0.30).

In this paper, we report a novel magnetic phenomenon quite different from that usually observed for such solid solution systems, namely, an antiferromagnetic (AF)–to-weakly ferromagnetic (WF) crossover phenomenon for UO_2–TiO_x heterogeneous multi-phase systems, $(1 - y)UO_2 + yTiO_x$ ($y = 0.05$–0.72, $x = 0$(Ti), 1.0(TiO), $1.5(Ti_2O_3)$ and $2.0(TiO_2)$). The present samples were prepared by the usual ceramic method, using high-purity TiO_x powders (Soekawa, 99.9% for $x = 0$, 1.0 and 1.5, and 99.99% for $x = 2.0$), and UO_2 powder obtained from chemically pure-grade uranyl nitrate as starting materials [5]. The pellets of these starting mixtures were high-temperature heat treated at 1300–1500°C in an

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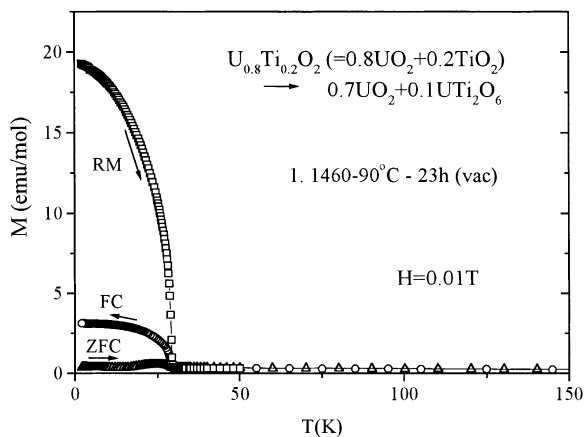*E-mail address:* nakamura@analchem.tokai.jaeri.go.jp (A. Nakamura).

Fig. 1. Magnetization (M) vs. temperature (T) plot of $0.8UO_2 + 0.2TiO_2$ multi-phase system ($x = 2.0$, $y = 0.2$) at $H = 100\,G$ (0.01 T) after heat treatment at 1460–1490°C for 23 h in vacuum. Three curves measured in the ZFC mode ($\triangle$), FC mode ($\bigcirc$), and RM mode ($\square$) after returning H to 0.01 from 5.5 T at 2 K, are shown.

Fig. 2. (M(RM)) at 2 K vs. Composition (y) plot for $(1 - y)UO_2 + yTiO_2$ system ($x = 2.0$). Arrows ($\rightarrow$) at $y = 0.5$ and 0.67 indicate M(RM) after the first and second heat treatments. Error bar at $y = 0.20$ indicates the maximum deviation of M(RM) for three samples from different specimen portions.

induction furnace in a vacuum better than 10^{-5} Torr. Their powder X-ray diffraction (XRD) analyses showed that the only compound formed is UTi_2O_6 (brannerite at $y = 0.67$) between UO_2 and TiO_2 ($x = 2.0$), and almost no solubility of TiO_x ($x = 0$, 1.0, 1.5 and 2.0) into UO_2 was detected (no measurable lattice-parameter ($a_0 = 0.5470$–$0.5480\,nm$) shift of UO_2). Accordingly, their phase compositions are judged to be, for $x = 0$, 1.0 and 1.5, a heterogeneous two-phase mixture of $UO_2 + TiO_x$ for all the y and for $x = 2.0$, that of $UO_2 + UTi_2O_6$ for $y < 0.67$ and for $y > 0.67$ that of $UTi_2O_6 + TiO_2$ plus minor residual UO_2. Thus, as evidenced by the magnetic susceptibility measurements, UTi_2O_6 could not be prepared as a single-phase material even at $x = 0.67$ using the present heating conditions. Electron probe microanalyses (EPMA) were also performed for three selected systems exhibiting the most pronounced AF–WF crossover phenomenon. This was done in order both to examine the microstructure of these multi-phase systems and to check whether this phenomenon originates from the existence of some impurity phase not detected by the powder XRD method, that is, first, for the $0.5UO_2 + 0.5TiO_{1.5}$ system ($x = 1.5$, $y = 0.5$), and second, for the $(1 - y)UO_2 + yTiO_2$ systems ($x = 2.0$) with $y = 0.10$ and 0.20 (see Figs. 1 and 2). The former system ($x = 1.5$, $y = 0.5$) was indeed confirmed by EPMA methods to be a heterogeneous two-phase mixture of the starting UO_2 and Ti_2O_3. And the latter two systems ($x = 2.0$, $y = 0.10$ and 0.20) were found to have several characteristic microstructures associated with the formation of the above-mentioned brannerite phase 'UTi_2O_6'. This will be discussed later in connec-
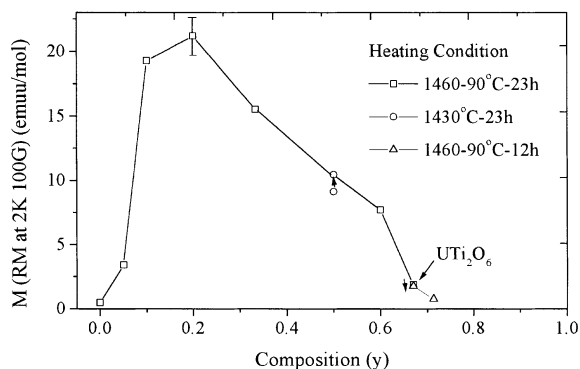
tion with their magnetic properties. DC magnetic susceptibility (χ) measurements were performed using a SQUID magnetometer (Quantum Design, MPMS) between 2 and 300 K and 0 and ± 5.5 T. First, the magnetic susceptibility of the present UO_2 powder was confirmed to exhibit a nearly identical sharp drop at T_N ($= 30.5\,K$) before and after the heat treatment over the field (H) range of 0.01–5.5 T, as reported previously on this system.

In contrast, the magnetic susceptibilities (χ) of these multi-phase systems were found to exhibit a sharp upturn (increase) at their respective T_N values, while T_N decreased only slightly (at most from 30.5 to 29.0 K) with increasing y. Fig. 1 shows a typical example of such behavior for the $0.8UO_2 + 0.2TiO_2$ system ($x = 2.0$, $y = 0.20$) measured at $H = 0.01$ T, where the largest remanent magnetization at 2 K (M(RM)) among all the systems studied so far was found. The approximate phase composition of this system deduced from the XRD analysis is $0.7UO_2 + 0.1UTi_2O_6$. The χ-upturn phenomenon at $T_N = 29.3$–$29.8\,K$, which is slightly lower than 30.5 K for $y = 0$, is commonly observed for all the ZFC (zero-field cooled)-, FC (field cooled)- and RM (remanent magnetization) modes. The magnitudes of the χ-upturns appear consistently in the order RM $\gg$ FC > ZFC, clearly exhibiting the switchover to a WF transition at T_N and the growth of a ferromagnetic hysteresis loop with decreasing temperature below T_N in this system. The latter was indeed confirmed by isothermal magnetization (M) vs. H measurements between ± 5.5 T at several temperatures below T_N. Fig. 2 shows the trend of remanent magnetization at 2 K and 0.01 T (M(RM)) as a function of composition (y) for $(1 - y)UO_2 + yTiO_2$ systems ($x = 2.0$). A very clear and reproducible variation of M(RM) is seen here. As y increases from zero, M(RM) of the system rapidly rises to a maximum around

$y \sim 0.10$–0.20, then tends to decrease gradually, and finally this AF–WF switchover phenomenon almost disappears around and beyond $y \sim 0.67$, the point at which UTi_2O_6 (brannerite) is formed. Careful EPMA analyses of the two systems exhibiting the largest M(RM) ($y = 0.10$ and 0.20) in Fig. 2 show basically the same UO_2–UTi_2O_6 two-phase structure as deduced from the XRD analysis (the average grain size of UO_2 is $\sim 20\,\mu m$ for $y = 0.10$ and $\sim 15\,\mu m$ for $y = 0.20$). But, occasionally, a two band-like structure of the UTi_2O_6 grains was found, the two plausibly corresponding to the Ti-rich (Ti/U > 2.0) and stoichiometric (Ti/U = 2.0) brannerite, respectively. In addition, in other portions, many fine UO_2-segregated stripes were observed running inside the UTi_2O_6 grains in both of these systems. These observations seem to indicate that this brannerite phase can accommodate nonstoichiometric (variable) Ti/U composition, $U_{1-z}Ti_2O_6$ (both $z > 0$ and < 0), at high temperature, the homogeneity range of which would narrow with decreasing temperature, causing a complex phase-separation behavior when cooled to room temperature. However, to what extent these UO_2 stripes (and also the two-band like structure) inside the UTi_2O_6 grains are responsible for their large M(RM) needs further examination. This is because, as mentioned earlier, the $0.5UO_2 + 0.5TiO_{1.5}$ system ($x = 1.5$, $y = 0.5$), which does not form such a UTi_2O_6 (or any other) intermediate phase and is indeed almost a complete two-phase mixture of the starting UO_2 and $TiO_{1.5}$, also exhibits relatively large M(RM) (= 12.5). This χ upturn at T_N is pronouncedly observed for UO_2 having Ti-oxide (titania) partners TiO_x ($x = 1.0(TiO)$, $1.5(Ti_2O_3)$ and $2.0(TiO_2)$) over a wide composition (y) range above $y \sim 0.10$. In such optimized cases, this χ upturn at T_N extends up to $H = 3$–$4\,T$ region at maximum, and only above $\sim 5\,T$ is the original antiferromagnetic χ drop at T_N, as observed for pure UO_2, recovered. It is noteworthy that for Ti metal ($x = 0$), the onset of the χ upturn at T_N is suppressed to a greater extent, both in its magnitude and in the range of field strength (H) for which it is observed. All of the experimental results obtained so far suggest that an AF–WF crossover phenomenon is induced for UO_2–TiO_x multi-phase systems, especially for the Ti-oxide partners, plausibly owing to the magnetic and/or quadrupole modification of UO_2 at the interface region in contact with the oxide partners. The detailed nature and origin of this new finding, however, will have to be clarified in future studies.

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