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Microhardness study of some novel compounds and alloys

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Vickers microhardness has been measured at room temperature on a numerous compounds and alloys containing Ce (4f) and/or U (5f) metals (all together on 43 samples with different compositions represented by the parameter x) belonging to the following series of systems: $Y_{1-x}U_xRu_2Si_2$, $Ce_{1-x}Y_xRu_2Si_2$, $Ce_{1-x}Y_xCu_{2.05}Si_2$, $Ce_{1-x}La_xCu_{2.05}Si_2$, $Ce_{1-x}U_xAl_2$, $Ce_{1-x}U_xNiSn$. The significant changes were observed for all examined series of the systems with the discernible maximum or minimum in the recorded hardness curves. Whereas the maximum could be easily explained by the available theories, explanation of the minimum needs additional studies. © *2004 Kluwer Academic Publishers*

1. Introduction

By 1980's of the last century various technological advances have enabled producing pure 4f and 5f elements that opened possibilities for the preparation (and characterization) of some novel compounds and alloys [1]. Unfilled atomic levels of 4f and 5f ions are responsible for the vast novel phenomena observed and properties discovered on the examined systems. New concepts and terms such as heavy fermion compounds, mixed valence compounds, intermediate valence compounds, valence fluctuation, etc., have been envisaged and theories put forward. The present study was motivated by the mentioned scientific conjectures and because little attention has been paid to the mechanical properties of such materials so far. One of the reasons for that is certainly connected to the problem of the sample preparation procedures and the quality of samples. Various routes of sample preparation do not allow one to compare mechanical properties among different systems. In some cases the samples are not sufficiently homogeneous and do not allow determination of their intrinsic mechanical characteristics within even the same system. Here we present, so far as we know, the first comprehensive study of mechanical behaviour of alloy systems containing Ce(4f) and/or U(5f) metals by means of the microhardness technique. Among many available methods for the investigation of mechanical properties the measurement of microindentation hardness (or microhardness) is a very convenient and useful technique [2–13]. It gives a quantitative indication of the strength of the material, especially its resistance to their plastic deformation or to the movement of dislocations. So, in the present paper we report the results of microhardness measurements on samples prepared from six series of cerium and/or uranium alloy systems and show that the microhardness is an effective parameter. Then we tried to answer if the obtained results reflect intrinsic properties of the examined systems or the results are greatly influenced by the method of preparation of the samples or the materials are not in solubility regime. Finally, we have compared the results obtained to the results of the microhardness investigations on the other systems, and correlate them with the available theories.

2. Experimental

The microhardness of the following nominal compositions (expressed by the parameter x) of the six series of the alloy systems were studied in order to gain an overall picture of behaviour: $Y_{1-x}U_xRu_2Si_2$ (with $x = 0, 0.08, 0.3, 0.5, 0.66, 0.89, 1$), $Ce_{1-x}Y_xRu_2Si_2$ (with $x = 0.05, 0.1, 0.6, 0.75, 0.9, 0.95$), $Ce_{1-x}Y_xCu_{2.05}Si_2$ (with $x = 0.05, 0.3, 0.5, 0.7, 0.9, 1$), $Ce_{1-x}La_xCu_{2.05}Si_2$ (with $x = 0, 0.02, 0.05, 0.1, 0.2, 0.3, 0.4, 0.5, 0.7, 0.9, 0.98$), $Ce_{1-x}U_xAl_2$ (with $x = 0, 0.05, 0.1, 0.2, 0.79, 0.9, 0.98, 1$) and $Ce_{1-x}U_xNiSn$ (with $x = 0, 0.1, 0.15, 0.2, 0.3$). After weighing a proper contents of the constituent metals, they were melted together in an arc-melting furnace. The liquid master alloy was sucked in to a mold where it was allowed to cool slowly. The prepared shape of the samples, a rod of about $1 \times 1 \times 10$ mm^3, was suitable for transport properties measurements

[13–15], and also the same samples were taken for microhardness measurements. The exceptions were the alloy systems $Ce_{1-x}Y_xCu_{2.05}Si_2$ and $Ce_{1-x}La_xCu_{2.05}Si_2$; in these cases the master alloys, after melting and solidification, were cut into suitable shape. Finally, the samples were annealed for different time intervals at various temperatures in order to achieve homogeneous and single-phase material. The formation of a continuous series of solid solution, i.e., a single-phase alloy with the tetragonal structure, was confirmed by X-ray diffraction method. However, the X-ray diffraction method indicated small traces of a second phase in all samples of the $Y_{1-x}U_xRu_2Si_2$ alloy system. Indeed, the microstructure and elemental composition of the alloy have been analyzed using scanning electron microscope (SEM, Jeol JSM 5800) and energy dispersive X-ray spectroscopy (EDXS, Oxford—Link ISIS 300). Both SEM and EDXS analysis have shown that beside the main phase there exists a small amount of a second phase embedded in the matrix. A detailed analysis of these investigations will be given elsewhere. We also note that there is the miscibility gap around $x = 0.5$ for the systems $Ce_{1-x}Y_xRu_2Si_2$, $Ce_{1-x}U_xAl_2$ and $Ce_{1-x}U_xNiSn$. After transport property measurements the samples were mounted in an epoxy resin holder to be handled easier during a standard polishing procedure, and during microhardness measurements. The microhardness data were collected at room temperature using an E. Leitz (Wetzlar, Germany) Miniload type II aparatus with a Vickers (136°) diamond pyramide indenter. For the results described in this paper the problem of the choice of indenter load was carefully considered. This was done because of the experimental fact that measured microhardness depended on the load applied to the indenter during measurements, and the examined materials here are not an exception. We chose a load of 0.981 N as a compromise between the accuracy consideration and experimental fact that microhardness for loads exceeding this value become independent of load within the experimental error. The loading time was 10 s, and at least 20 indentations were made for each microhardness value reported here. In our microhardness measurements the values of the standard deviation were close to 10% (on average) of the mean hardness values. Finally, we would like to note here that some samples were brittle and microhardness measurements on these samples were performed carefully. The length of the indentation diagonal in the above cases was less reproducible due to the cracking.

3. Results and discussion

The main features of the microhardness behaviour in the alloy series examined can be understood from Fig. 1. On the figure each point corresponds to a different sample. Also, the error bars, which amounted (to approximately) 10%, were omitted for clarity. From the same figure one may conclude that the metal X dissolved in a compound of metal Y normally causes an increase or a decrease of the hardness of alloyed compound Y, and conversely. This is in agreement with the fact that we are

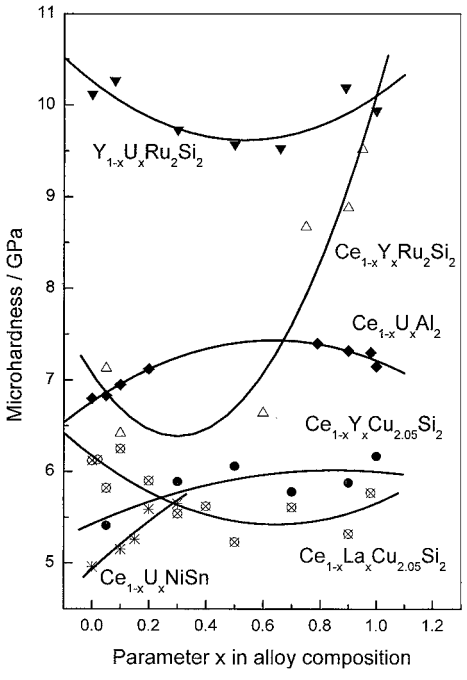

Figure 1 Variation of Vickers microhardness with the parameter x. (x expresses a series of compositions of the alloy systems examined).

dealing with systems containing various kinds of atoms and their sizes. Consequently the hardness-composition curve for a continuous series of solid solution prepared from X and Y components generally rises-up to a maximum or goes-down to a minimum at some position between the values for the two components. A typical example for the appearance of such maximum has been observed on the series of gold and silver system examined by N. Kurnakov *et al.* (see Fig 5.5 in [17]); in this case he has got a maximum value practically twice as great as that of either of the pure metals. According to the authors' present knowledge there are only a few examples for the systems that microhardness-composition curve exhibited a minimum. This may occur only for the so called terminal solid solution; whereas, if solute component becomes richer the curve again raises-up. In contrast, it is interesting to note here the work of J.H. Westbrook who has investigated microhardness behavior of the system Ag-Mg at various homologous temperatures (T/T_m, with T_m equals to melting point temperature) versus composition of Mg component (see Fig. 39, which has appeared in the Hassen's paper [16]). Namely, below some critical temperature hardness-composition curves show a maximum, whereas above this temperature they show a minimum. Explanation of the observed minimum on microhardness-composition curve given there might be valid here. However, here we put forward another possible explanation. Approaching melting point a material becomes less hard. The melting points of our systems were not known. Nevertheless, it is reasonable to assume that T_m passes through a minimum about the middle of a series due to increasing of disorder. Therefore the measurements at room temperatures we performed means that we are closer to melting point for the alloys in the middle of a series and, therefore, in some cases we observe a minimum in microhardness. However, at present

we are not able to give definite explanation for this effect.

The curves drawn in Fig. 1 are obtained using the polynomial (quadratic) least square fit to the experimental data. The calculated curves fit the data quite well and they show that microhardness exhibits maximum or minimum almost at the middle of the composition ($x \sim 0.5$) of a series. This fact together with the relatively small standard deviation suggests that we have measured intrinsic microhardness. At the moment it is not clear to us why the microhardness of $Y_{1-x}U_xRu_2Si_2$ is the highest among the investigated systems. This could be explained by the presence of the minor amount of the second phase in the samples, which can be pinning centers for the dislocation movement; or, on the other hand, the electronic properties are different in that system in the sense that this system exhibits some semi-metallic properties that could lead to higher microhardness.

4. Conclusions

The following conclusions can be drawn so far:

(i) Single-phase polycrystalline samples of the alloy systems: $Ce_{1-x}La_xCu_{2.05}Si_2$, $Ce_{1-x}Y_xCu_{2.05}Si_2$, $Ce_{1-x}U_xRu_2Si_2$, $Y_{1-x}U_xRu_2Si_2$, $Ce_{1-x}U_xAl_2$ and $C_{1-x}U_xNiSn$, i.e., the systems that contained Ce(4f) and/or U(5f) metals, were successfully prepared by the argon arc-melting furnace, and microhardness measurements were performed on them.

(ii) Comparison of the results represented in Fig. 1 evidenced discernible difference in the microhardness behavior of the examined alloy series that is outside of the experimental errors.

(iii) The observed maximum on some microhardness curves could be explained by the existing theories (e.g., Mott-Nabarro theory); whereas the minimum observed for $Y_{1-x}U_xRu_2Si_2$ $Ce_{1-x}Y_xRu_2Si_2$ and $Ce_{1-x}La_xCu_{2.05}Si_2$ needs additional studies to elucidate.

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