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Abstract
We show that the Vickers microhardness, measured on flux grown single crystals of the $Yb_xY_{1-x}InCu_4$ alloy system, although sample dependent, exhibits clear concentration dependence; it increases with decreasing x. Such a dependence is not expected because the cubic lattice parameter increases with decreasing x and one expects then a decrease of hardness with decreasing x. Also, such a concentration dependence is in accordance with neither the Mott–Nabarro theory nor other known experimental results. We ascribe the observed dependence to the change of the electronic structure of the $Yb_xY_{1-x}InCu_4$ alloy system with x.

1. Introduction

By the 1980s, various new technological processes had enabled the production of pure 4f and 5f elements, and this opened possibilities for the preparation and modelling of compounds and alloys with scientifically interesting and novel properties [1]. Partially filled atomic levels of 4f and 5f ions are responsible for such diverse phenomena as unconventional superconductivity, heavy-fermion and valence-fluctuation characteristics, small moment interactions, Landau liquid ground state and many other interesting and not yet explained phenomena. The present study was motivated by the existence of such phenomena and because little attention has so far been paid to the mechanical properties of such materials, although it is probable that partially filled f atomic levels will influence the mechanical properties of alloys and compounds containing such elements. It is known that d transition elements and systems containing them display increased hardness due to the existence of partially filled d levels, which increase the cohesive forces between ions. A detailed study of this phenomenon is usually limited by the low solubility of d elements, again because of the character of the d orbital, which is rather extended in space, and such elements make various intermetallic compounds easily. Therefore, increased

hardness in the plastic regime is in many cases a result of pinning dislocations on precipitates or due to small regions of second phase material, not intrinsic pinning due to partially filled d orbitals. The spatial extent of f orbitals is reduced relative to d orbitals, and this fact enhances solubility, i.e., mixing with a nonmagnetic ion in a wide concentration range. Therefore, one may expect to investigate the influence of changes in electronic structure on hardness in such systems.

Variations in experimental techniques for fabricating samples limit comparisons of mechanical properties across different alloy systems, and in many cases synthesized samples are not sufficiently homogeneous to allow the determination of intrinsic mechanical properties within even a single alloy series. This is especially true in the early development of novel materials systems, which are often first obtained in polycrystalline form, and this has limited the extent of mechanical properties investigations in such systems. Nevertheless, recently we have performed mechanical investigations of several polycrystalline alloy systems containing U (5f) and Ce (4f), all prepared by an arc-melting method, by means of the microhardness technique [2]. We have shown that there is a certain consistency of the results and that the results are not so sample dependent as one might fear. Moreover, some of these results can be explained within existing theories.

Among many available methods of investigation of mechanical properties, microhardness or micro-indentation hardness testing seems to be a very convenient and useful technique, which gives a qualitative indication of the strength of a material, especially its resistance to plastic deformation, i.e., to the movement of dislocations. It is well established that microhardness pyramidal testing yields values which are approximately three times higher than the yield stress of a specimen which received 8% previous reduction by cold-work [3]. One may ask whether this result, which depends upon dislocation and slip movement, bears any relation to the cohesive forces that bind atoms together, or, ultimately, with the electronic structure. Empirically, there are a number of experimental results that show correlations between microhardness and other physical properties such as Young's modulus, atomic size, melting point, and, indirectly, cohesive forces [3].

In this work we present our microhardness study of the $Yb_xY_{1-x}InCu_4$ alloy system. As the preparation of the monocrystalline samples of this alloy system appears rather uniform, we expected that the results of microhardness measurements would reflect the characteristics of the electronic structure of this system, the evolution of which are an active area of study in this system [4].

2. Experimental details

A detailed description of the preparation of monocrystalline samples of the $Yb_xY_{1-x}InCu_4$ alloy system is given in [5]. The cubic $C15b$ (MgCu$_4$Sn-type) crystal structure is retained throughout the entire series and the Yb and In atoms are located at the face-centred positions and are in a zincblende-type arrangement.

For the microhardness measurements the samples were mounted in an epoxy resin holder to facilitate handling during a standard polishing procedure. The microhardness testing was performed at room temperature using a standard E Leitz (Wetzlar, Germany) Miniload II apparatus supplied with a 136° diamond pyramid indenter. Initial experiments revealed that microhardness data depended on the load applied on the indenter, but for loads exceeding roughly 0.981 N microhardness was nearly independent of load. Therefore, the load of 0.981 N, so-called HV 0.1, was selected as the standard value for microhardness measurements. The loading time was 10 s. The magnification used in microhardness measurements was constant and equal to 500×.
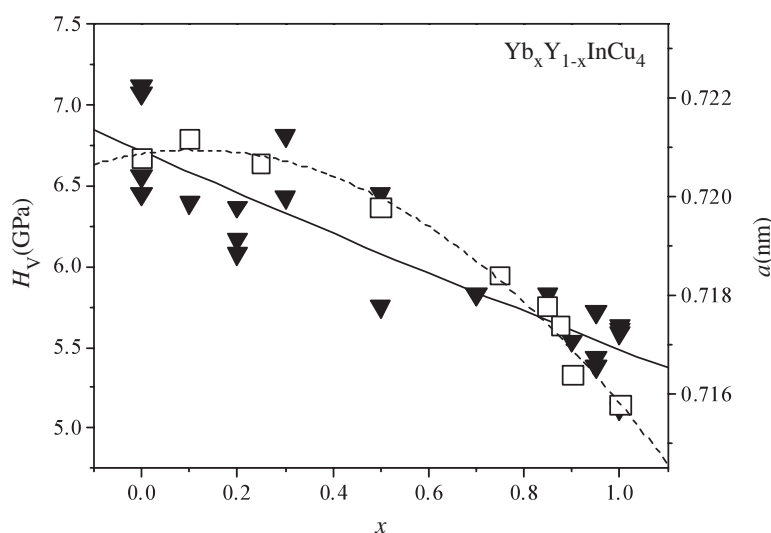
Figure 1. The microhardness (triangles) and lattice parameter (squares) of the $Yb_x Y_{1-x} InCu_4$ alloy system. The lines are polynomial fits of the second order and they are drawn only as guides to the eye through the microhardness data (full line) and lattice parameter data (dashed curve).

In order to obtain the average value of microhardness, twenty indentations were made on each examined sample. For each sample, the standard deviation was always less than 10% of the mean value. In addition, for the samples having the same composition, the largest difference in the calculated mean values, see figure 1 for $x = 0.5$, was also about 10% of their mean values. As the standard deviation of the measurements on each sample is also about 10%, we conclude that the main error comes from the errors in the measurements and perhaps due to the difference of preparing the surface by polishing, but not due to some essential difference between the samples. Some samples were brittle, especially for lower x. For these concentrations, the length of the diagonal of the indent was less reproducible because of cracks around indentations. The traces of indents which deviated slightly from quadratic form were not taken into account.

3. Results and discussion

In figure 1, we display the results of microhardness measurements for the $Yb_x Y_{1-x} InCu_4$ alloy system (triangles) together with lattice parameter data (squares). The lines represent polynomial fits of the second order and are drawn only as guides to the eye through the microhardness data (full line) and lattice parameter data (dashed line). Nevertheless, these lines suggest that there is not a direct connection between the microhardness and lattice parameter data.

According to the Mott–Nabarro theory, the hardness of a binary alloy system with atoms of different sizes should have a maximum at 50% at about $x = 0.5$. Our results show clearly that Yb and Y are not equivalent and that they do not behave like hard spheres [6].

According to a Rydberg study, one can correlate hardness with the reciprocal of the size of the atoms for pure elements [3]. This conclusion and the underlying experimental results follow, in principle, from the view that the hardness is proportional to the cohesive forces. In our case, the hardness is roughly proportional to the lattice parameter (and not its reciprocal)

and, therefore, our results cannot be explained by this ansatz. Intuitively, the hardness is proportional to the density of a material. Again, our results are not in accordance with this expectation. Our system is less dense for lower x not only because the lattice parameter increases with decreasing x, but also because yttrium is lighter than ytterbium.

In a study of ultrarapidly quenched 3d transition elements in Al, it was shown that the microhardness is proportional to the deviation of the lattice parameter from Vegard's law [7]. At present these results are understood in the following picture. The deviations from Vegard's law are an indication that the nominal concentration of transition metal atoms did not in fact substitute for Al in the lattice, although the cited study investigated only low alloy concentrations believed to be in the solubility region for the transition atom in the Al matrix. Such transition element atoms which are not included into substitution positions probably form precipitates in the sample. The small volume concentration of precipitates cannot be observed by the Debye–Scherrer method, which was used for the examination of the crystal structure and for the determination of the lattice parameters of the alloys. It is known that precipitates are rather effective in pinning dislocations, producing considerable enhancement of microhardness.

At first glance, a similar effect might be indicated in the present investigation. A nonlinear behaviour of the lattice parameter is observed, and, moreover, a faint maximum is apparent at about $x = 0.1$, inconsistent with the Vegard's law expectation. However, here these deviations can be shown to be intrinsic and result from the homogenous mixing of the Yb^{3+} and Yb^{2+} ions, and the maximum is due to a relatively enhanced mixing at low concentrations. As there is a difference of ionic volumes between Yb^{3+} and Yb^{2+}, the results of [7] and the Mott–Nabarro theory would suggest an enhancement of microhardness at lower concentrations. However, this model still cannot explain why $YInCu_4$ displays larger microhardness than $YbInCu_4$; the Mott–Nabarro approach would imply that the microhardness of $YInCu_4$ and $YbInCu_4$ should be the same.

Recently a comprehensive investigation of the $Yb_x Y_{1-x} InCu_4$ alloy system has been reported [4]. One of the conclusions coming from this study is that the alloy system evolves from semimetallic towards more metallic character with increasing x. Band calculations for $LuInCu_4$ indicate that the Fermi surface consists of a hole and an electron band with the Fermi energies $\varepsilon_F^h = 0.192$ and $\varepsilon_F^e = 0.592$ eV around W and X symmetry points respectively [8]. With increasing lattice parameter, band overlap and Fermi energies decrease. In fact, resistivity data do suggest that the Fermi energy for $YInCu_4$ might be of the order of room temperature. On the other hand, with decreasing lattice parameter, band overlap increases and the bandwidth of $YbInCu_4$ has been estimated to be about 5000 K. In accordance with this picture of the $Yb_x Y_{1-x} InCu_4$ alloy system, we believe that the microhardness data displayed in figure 1 reflect this change of the electronic structure in $Yb_x Y_{1-x} InCu_4$ from semimetallic towards more metallic character. It is known that insulators and semimetals are harder then metals. For example, in the group IV elements C, Si, Ge, Sn, Pb, Bi, where metallic character increases with increasing atomic number, microhardness decreases: 78.5, 12.1, 5.4, 0.061, 0.031, 0.171 GPa, respectively (we note that Bi is again a semimetal due to its 'nonmetallic' crystal structure) [9]. In this view the f states of Yb seem to play no significant role on hardness. The decrease of the lattice parameter with x comes from the fact that Y^{3+} is larger than Yb^{3+}. The band calculations in [8] for $YbInCu_4$ show that the f states of Yb are close to the Fermi level and, thus, they should increase the cohesive forces with increasing x. However, it seems that the microhardness data still confirm one conclusion from the investigation reported in [4]. This investigation was undertaken to determine the strength of Kondo interactions in $Yb_x Y_{1-x} InCu_4$. It was shown that clear Kondo character may be associated with low concentration alloys and that the Kondo temperature is about 2 K. That means that the f states are not necessarily at the Fermi level (FL)

and might only contribute to the formation of the Abrikosov–Suhl many-body resonance at the FL with weak f-conduction electron mixing.

Finally, we should discuss how to connect the electronic properties we believe that the microhardness of $Yb_xY_{1-x}InCu_4$ reflects with the dislocation picture, which is responsible for the mechanical properties in the plastic regime. There is no reason in the synthesis of the samples that would produce more dislocations for higher concentration of Yb resulting in lower microhardness. One might expect enhanced numbers of dislocations for x about 0.5. We do see that just for $x = 0.5$ there is the largest difference in the microhardness between our two samples. Due to the enhanced mixing of the Yb^{3+} and Yb^{2+} ions at lower concentrations one could expect there to be an increase in the number of dislocations. However, the microhardness data do not confirm such expectations. Thus, we assume that the number of dislocations is essentially uniform throughout the series and that this number could depend more on extrinsic details of a particular sample and not on the concentration. Nevertheless, as discussed in the section devoted to the experiment and to the errors of the measurements, the experimental results do not allow us to draw such a conclusion. Therefore, in our picture the dislocation movement depends on the strength of the connection between the ions making the alloys, which are stronger in the case when the alloys exhibit more semimetallic character.

Direct connections between microhardness, i.e., mechanical properties in the plastic regime, and electronic properties are very difficult to identify and are rarely studied. Nevertheless, the concentration dependence of microhardness in the $Yb_xY_{1-x}InCu_4$ single crystals alloy system appears to reflect just such a connection: in particular decreasing microhardness as the system evolves from semimetallic towards more metallic character. We have also shown that the f states of Yb, which are responsible for a large number of novel and interesting electronic and thermodynamic properties, do not appear to play an important role in the plastic regime of mechanical properties in this system.

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