Synthesis of CaMg-based bcc alloys and their hydrogenation properties

Tohru Nobuki [a], Masafumi Chiba [a], Toshiro Kuji [b],*

[a] *School of High Technology for Human Welfare, Tokai University, Japan*
[b] *Course of Materials Science and Chemistry, Unified Graduate School, Tokai University, 317 Nishino, Numazu-city, Shizuoka 410-0395, Japan*

Abstract

We have demonstrated in our previous reports that the excess energy created during mechanical alloying (MA) yielded alloying of couples with even positive mixing enthalpy forming new ternary bcc phases. It was noticed that the important issue there was the structural correlation between the Laves and bcc structures. In this study, we successfully synthesized new ternary $CaMg_2X$ (X = V, Fe, Mo) bcc alloys from the viewpoint of the structure correlation between $CaMg_2$ Laves and the bcc elements. It was found that the mechanical alloyed bcc phases were composed of nano-structured bcc grains and the synthesized alloys were able to absorb hydrogen.
© 2007 Elsevier B.V. All rights reserved.

1. Introduction

It is well-known that the mechanical alloying technique is useful to fabricate alloys with nano-structural morphology [1,2]. Over the last several years, we have reported that the excess mechanical energy created during mechanical alloying process is able to compensate for a positive mixing enthalpy [3,4]. Mechanical alloyed materials show not only nano-structural morphology but also new functionality such as hydrogen absorption and magnetic characteristics [5]. As a result, it can be concluded that the mechanical alloying process is promising for the fabrication of alloys with multifunctional properties.

In our group, attention has been focused on the structural correlation between the Laves and bcc phases. In fact, TiCrV and TiFeV ternary bcc alloys could be assumed to be a solid solution of Laves phase in bcc elements [6]. This hypothesis was expanded into the non-equilibrium phase formation of Mg–X (X = V, Fe, Mo) couples with a positive mixing enthalpy.

In this study, therefore, we tried to demonstrate the dissolution of $CaMg_2$ Laves phase in bcc elements such as V, Fe, Mo by using mechanical alloying and studied their hydrogenation characteristics.

2. Experimental procedures

2.1. Materials and alloying

The nano-grained ternary bcc alloys were prepared from a highly purified ingot of $CaMg_2$ (Nihon Jyuka) and V (particle size, $s < 150\,\mu m$, purity, $p > 99.9\%$), Fe ($s < 100\,\mu m$, $p > 99.9\%$), Mo ($s < 80\,\mu m$, $p > 99\%$). Each bcc metal was produced by Koujyundo Kagaku. The powders were blended with a ratio of $CaMg_2$ to bcc elements in a 50:50 (at.%) ratio.

For the alloying, we used a stainless steel pot and balls with a vibration-type, high-energy Super Misuni NEV#8 (Nisshin Giken) ball mill. The alloying was performed at 710 rpm under an Ar atmosphere at room temperature. The alloying time was varied up to 60 h. The powder-to-ball weight ratio was 1:40.

2.2. Sample analysis

The powder mixtures were characterized by X-ray diffraction (MAC science MPX^3) with Cu Kα (operating at 40 kV–30 mA) and 2θ from 25° to 90°.

The SEM used was the Hitachi S-4000 with an acceleration voltage of 20 kV and equipped with a Horiba EMAX 2770 EDX spectrometer.

DSC (Rigaku DSC8230) measurements were carried out at a heating rate of 20 K/min under an Ar gas atmosphere.

The lattice image and diffraction pattern were determined using high-resolution TEM (Hitachi FE-TEM HF-2200TU) with an acceleration voltage of 200 kV after preparation by FIB (Hitachi FB-2000A).

* Corresponding author. Tel.: +81 55 968 1211; fax: +81 55 968 1224.
E-mail addresses: nobuki@urchin.fc.u-tokai.ac.jp (T. Nobuki),
tkuji@urchin.fc.u-tokai.ac.jp (T. Kuji).

The saturation magnetization of powdered samples was determined by a vibrating sample magnetometer (VSM) operating with a maximum magnetic field of 15 kOe at RT.

2.3. Hydrogenation

Hydrogenation was performed by high-purity, high-pressure hydrogen gas at 15 MPa and hydrogen desorption spectra were determined with a quadruple mass spectrometer during heating. The amount of absorbed hydrogen in the alloys was calculated from the corresponding hydrogen peak area.

3. Results and discussion

3.1. Mechanical alloying about $CaMg_2$–V

3.1.1. Chemical composition of bcc $CaMg_2V$ alloys

Fig. 1 shows the SEM images of the surfaces after different milling times for $CaMg_2$–V. This figure shows that the particle size becomes smaller with increasing mechanical alloying time. It can be seen that this mechanical alloying process proceeds via crushing and aggregating. Chemical composition analysis by the EDX spectrometer shows clearly that the composition of mixture did not change during mechanical alloying.
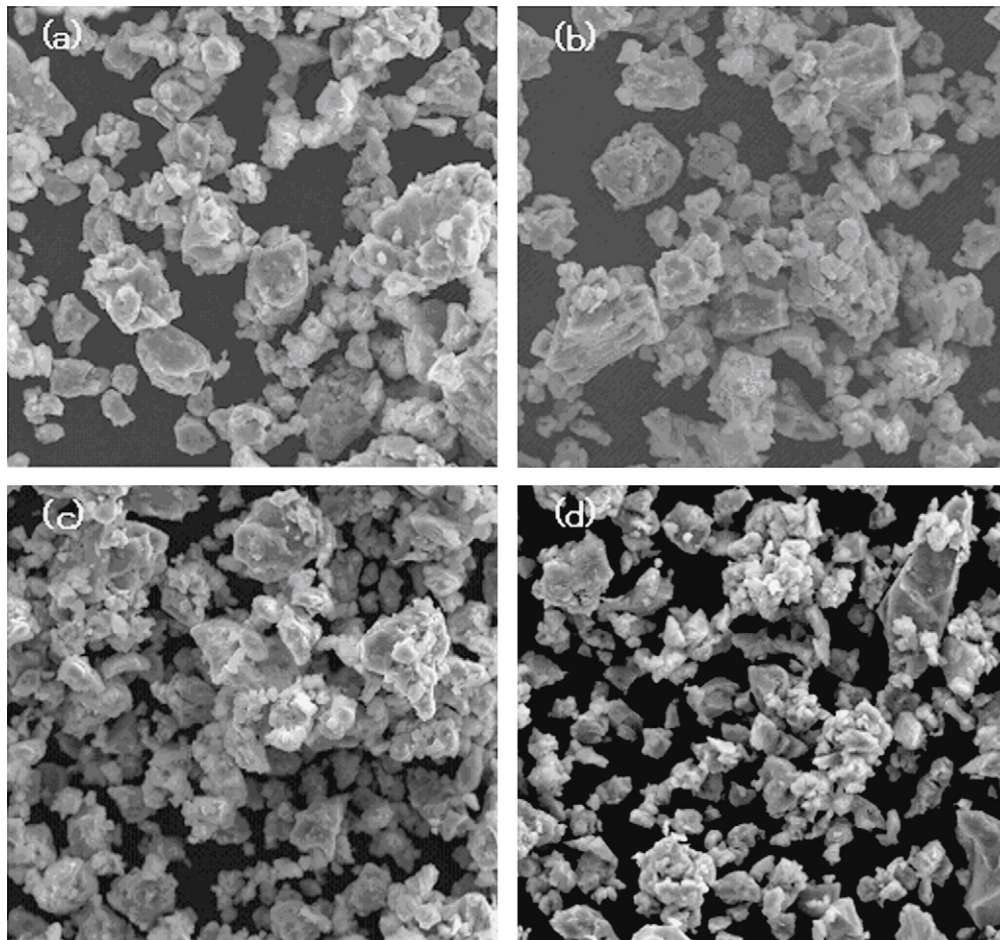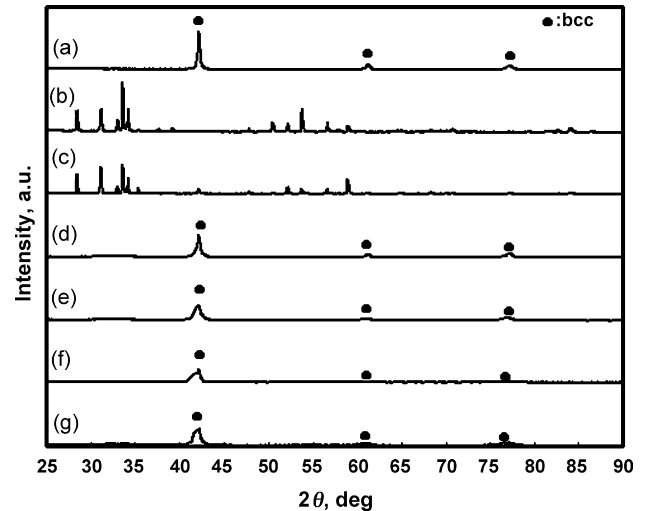
Fig. 2. The XRD patterns of $CaMg_2$–V mixtures with different mechanical alloying times. (a) V, (b) $CaMg_2$, (c) MA 0 h, (d) MA 10 h, (e) MA 20 h, (f) MA 40 h, and (g) MA 60 h.

3.1.2. Structure of synthesized alloys

Fig. 2 shows the XRD patterns of $CaMg_2$–V mixtures with different mechanical alloying times, indicating that diffraction

Fig. 1. The SEM images of the surfaces after different milling times for $CaMg_2$–V. (a) 10 h, (b) 20 h, (c) 40 h, and (d) 60 h.

peaks from $CaMg_2$ Laves phase disappeared in the initial stage of mechanical alloying, and then peaks from bcc of V broadened gradually with increasing mechanical alloying time. At 10 h of mechanical alloying, the XRD pattern was dominated by peaks from the bcc phase. In the case of mechanical alloying for 60 h, the XRD profile indicates that the mixture was composed of a single bcc phase. Thus, it can be concluded that the mechanical alloying for more than 20 h effectively transformed the mixtures to a bcc structure. The lattice parameter of the bcc alloys was measured from the XRD peaks. With increasing mechanical alloying time, the lattice parameter of the bcc alloy slightly expands, implying that the atomic radii of Mg and Ca are larger than that of V. This result indicates dissolution of Mg and Ca into the bcc V structure. It should be noted that Mg–V and Ca–V couples have positive mixing enthalpies, suggesting that it would be impossible to alloy these couples with conventional alloying techniques.

Hence, we can conclude that even if the mixing enthalpy ΔH_{mix} of an alloy is positive, the bcc alloy can be formed from the mixture of Laves phase and bcc elements using mechanical alloying.

3.2. Mechanical alloying for different X elements

In the cases of Fe and Mo elements, Mg–Fe(Mo) and Ca–Fe(Mo) couples have a positive enthalpy for mixing.

Fig. 3 shows XRD patterns for the cases of Fe and Mo elements obtained after 60 h of mechanical alloying. This figure indicates that a single bcc phase was formed after 60 h of mechanical alloying. This result suggests that the formation of Laves-related-bcc phases could be typical behavior. As shown previously in the case of $CaMg_2$–V, it was found again that increasing mechanical alloying time results in expanding the lattice parameter of the bcc alloy. But, the actual expansion value is very small.
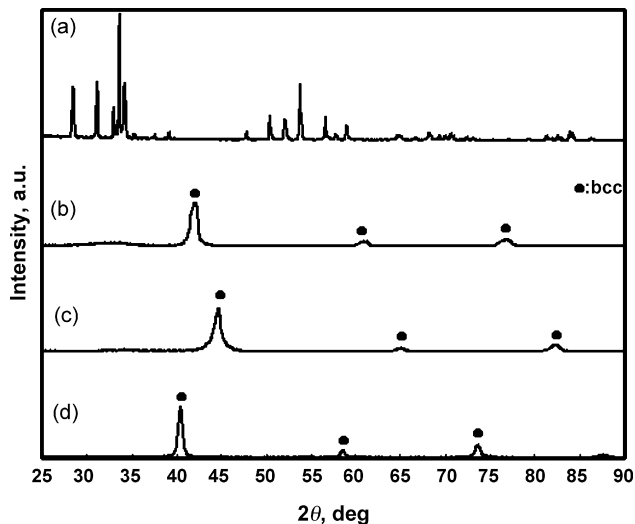
Fig. 3. The XRD patterns for the cases of Fe and Mo elements obtained after 60 h of mechanical alloying. (a) $CaMg_2$, (b) $CaMg_2$–V, (c) $CaMg_2$–Fe, and (d) $CaMg_2$–Mo.
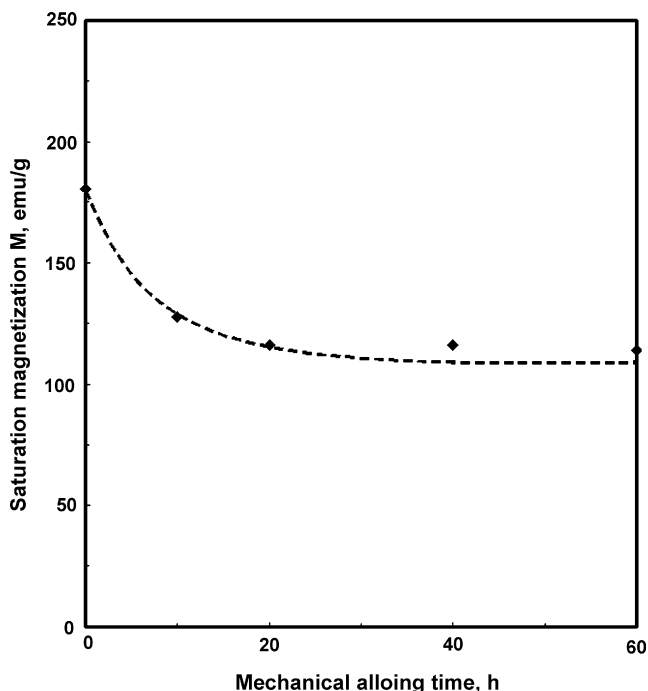
Fig. 4. The saturation magnetization of $CaMg_2$–Fe mixtures with mechanical alloying time.

Fig. 4 shows the saturation magnetization of $CaMg_2$–Fe mixtures with mechanical alloying time. This figure indicates that the saturation magnetization decreases with mechanical alloying time but was almost constant after 20 h, implying that the transformation is completed within 20 h of mechanical alloying. This result is consistent with the XRD results mentioned above.

In order to evaluate the fine structure of the alloys, TEM observations such as the lattice image and diffraction pattern were carried out. Fig. 5 shows the lattice image of $CaMg_2$–V alloy after 60 h of mechanical alloying. At first, the mean value of the chemical composition was collected from a 200 nm^2 area by EDX with TEM after sample preparation with FIB.

Fig. 5 shows the EDX images for $CaMg_2$–V. This figure shows that the alloy consists of nano-structured grains, and the deviations in elemental concentrations are negligibly small.

Fig. 6 shows the lattice image of $CaMg_2$–V after 60 h of mechanical alloying. This image indicates that the alloy consists of a crystallized structure, and the interplanar distance of the bcc alloy lattice was very close to the value in bcc V.

From the above results, we may conclude that the materials fabricated by mechanical alloying results in a nano-structured bcc alloy. The existence binary Laves phase combinations is very helpful for fabricating so-called Laves-related bcc phases [7,8].

3.3. Hydrogenation of $CaMg_2$–V, Fe and Mo alloys

From the DSC measurements about $CaMg_2$–V, the exothermic peak appears about at 240 °C. From this result, we determined to activate our alloys at 220 °C and 15 atm of hydrogen for 100 h in a reactor chamber. It was confirmed that the activation should be sufficiently long for hydrogenation.
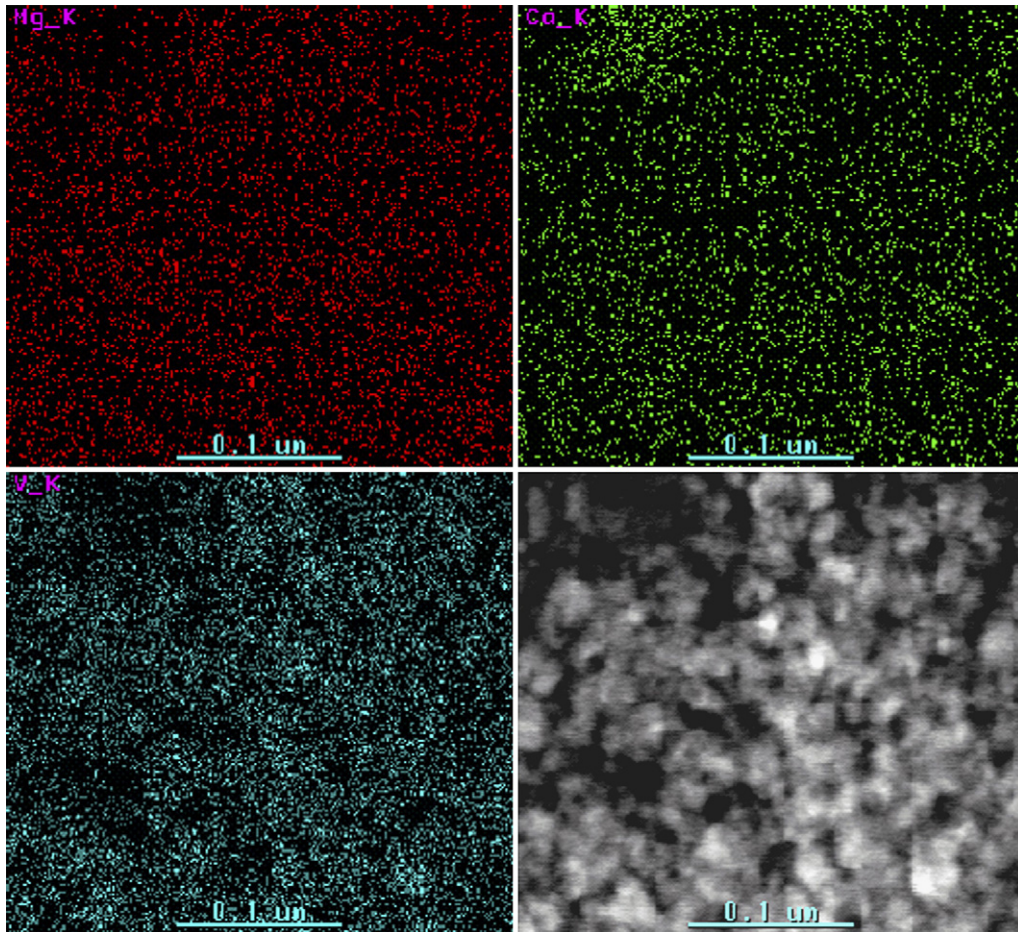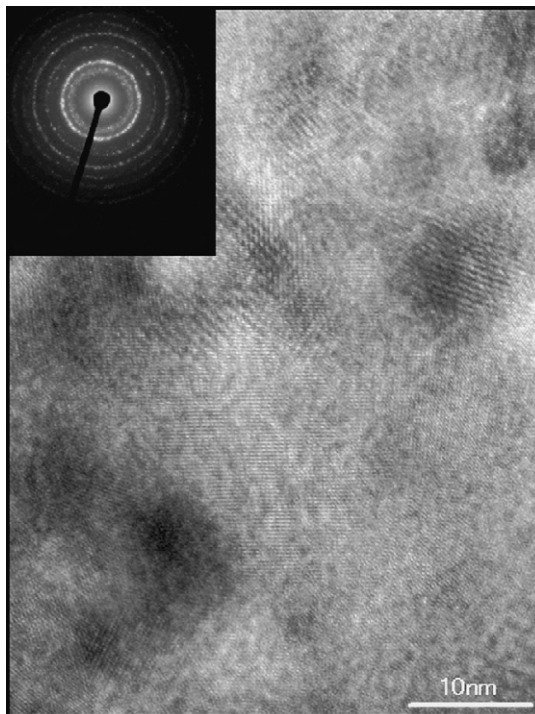
Fig. 5. The EDX images for CaMg$_2$–V.

Fig. 6. The lattice image of CaMg$_2$–V after 60 h of mechanical alloying.

Fig. 7 shows the TDS spectrum during heating from RT for the 60 h mechanically alloyed mixture. It can be seen that hydrogen desorption started at 330 °C and the peak temperature was 388 °C. The amount of hydrogen absorption in the alloy calculated from this spectrum was about 3 wt.%. On the other hand, in the cases of Fe and Mo, the quantities of absorbed hydrogen were calculated to be 1.5 wt.% and 1.0 wt.%, respectively.

This alloy structures were analyzed by XRD measurement before and after the hydrogenation. Hydrogenation seems to yield segregation of Mg because peaks from hydrides of Mg appeared. The above result indicates the Ca–Mg–V ternary bcc structure could not maintain after repeating absorption and desorption of hydrogen. However, it is difficult to conclude that the segregation was caused by hydrogenation alone. Segregation could also have been caused by extended thermal annealing during the hydrogenation process. The hydrogenation kinetics were very slow for the alloys prepared in this work, and the hydrogen was absorbed at relatively high temperature for a relatively long time. More studies are needed to clarify the reason the Mg segregation. The above behavior can be well explained by using Pauling's electronegativity. Our group has already reported synthesizing MgTmV (Tm = Ni, Co, Cu) alloys which could absorb a large amount of hydrogen even at RT [9,10]. The mean electronegativity values of the above alloys are approximately 1.42.
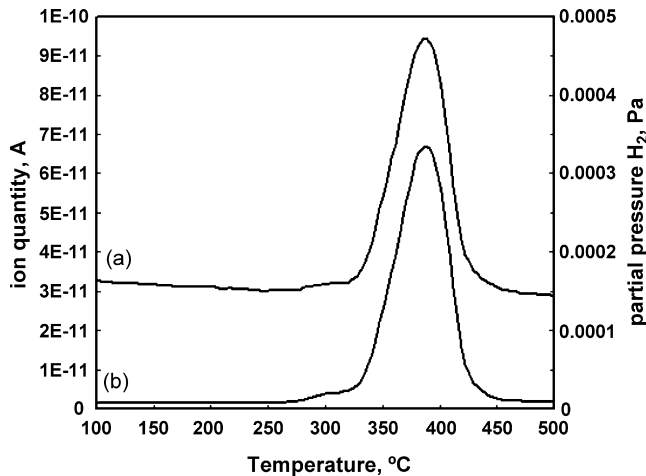
Fig. 7. The TDS spectrum during the heating from RT for a mechanically alloyed CaMg$_2$–V mixture for 60 h. (a) Ion quantity of H and (b) partial pressure of H$_2$.

The corresponding value of alloys in this study is 1.19 implying that the hydrides should be much were stable than MgTmV alloy hydrides. Especially both Ca and Mg hydrides are very much stable compared to V hydride. Therefore the difference in the stability of both hydrides seems not appear, although the electronegativity of V is far low from that of hydrogen.

The above results provide valuable information about hydride stability of non-equilibrium ternary bcc alloys, implying that selecting the elements for alloy design based on electronegativity is very useful because of the higher electronegativity elements could exhibit the instability of hydride.

4. Conclusions

Mechanical alloying was performed for mixtures of CaMg$_2$ Laves alloy and bcc elements of V, Fe, and Mo. The results are summarized as follows.

After 60 h of MA, a single bcc phase was formed for these mixtures. The TEM observation showed that such an alloy was composed of nano-structured bcc grains without deviation from nominal composition. Synthesized alloys could absorb large amounts of hydrogen, i.e., 3 wt.% of hydrogen for the case of bcc V. Although the phase segregation occurred after hydrogen desorption. This reaction can be explained by electronegativity argument of alloy elements relative to hydrogen. This result could encourage us to have a chance of new alloy phases.

Acknowledgements

References

[1] I. Borner, J. Eckert, Mater. Sci. Eng. 541–545 (1997) 226.
[2] H.Y. Leng, T. Ichikawa, S. Isobe, S. Hino, N. Hanada, H. Fujii, J. Alloys Compd. 404–406 (2005) 443.
[3] H. Hotta, M. Chiba, T. Kuji, H. Uchida, J. Jpn. Inst. Metals 70 (2006) 662–665.
[4] H. Yabe, T. Kuji, J. Metastable Nano Mater. 24–25 (2005) 439.
[5] H. Yabe, T. Kuji, J. Alloys Compd. 408–412 (2006) 313.
[6] H. Itoh, H. Arashima, K. Kubo, T. Kabutomori, K. Ohnishi, J. Alloys Compd. 404–406 (2005) 417.
[7] W. Sinker, Acta Mater. 44 (1996) 1623.
[8] Y. Zhang, Y. Tsushio, H. Enoki, E. Akiba, J. Alloys Compd. 393 (2005) 147.
[9] T. Kuji, S. Nakayama, N. Hanazawa, Y. Tabira, J. Alloys Compd. 356–357 (2003) 456.
[10] T. Kuji, H. Nakano, T. Aizawa, J. Alloys Compd. 330–332 (2002) 590.