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La-Al-Cu-Ni BULK METALLIC GLASS COMPOSITE

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Bulk metallic glasses possess superior mechanical properties with great potential for structural application. However, these materials failed by shear band. It is our aim to found new bulk metallic glass matrix composite with in-situ crystalline phase which can hinder the movement of shear band. Recently we have discovered in a La based alloy in which the fully amorphous formation is only 1.5 mm in diameter by chill casting, however, the glassy matrix composite with uniform distribution of La dendrites of more than 45% was found to be 12mm in diameter by copper mould chill casting. The critical cooling rate for fully glass formation was estimated to be >500 K/s and the critical cooling rate for the composite formation is then determined by Bridgman solidification to be around 15 K/s. Thermal analysis study of the fully amorphous and the composite samples indicates that the amorphous phase in the composite has a better thermal stability than that of the fully glassy sample. Here we will report the microstructural changes as a function of processing condition and their thermal and mechanical properties and the mechanism for such composite formation.

FORMATION, MICROSTRUCTURE AND PROPERTIES OF ZR-BASED BULK METALLIC GLASSES

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Various Zr-based bulk amorphous alloys (BAAs) were prepared. Some special methods were developed to improve glass forming ability and prepare the BAA with low purity of the elements under poor vacuum conditions. The glass forming ability and thermal stability, density, mechanical properties, acoustic velocities, and their temperature and pressure dependence have been investigated, and compared with those of oxide glasses and conventional amorphous alloys. The effects of the additions on the glass formation, and crystallization behavior are discussed.

EFFECTS OF ELECTROCHEMICAL HYDROGENATION OF ZR-BASED ALLOYS WITH HIGH GLASS-FORMING ABILITY

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Zr-(Ti)-Cu-Al-Ni metallic glasses exhibit a high thermal stability corresponding to a wide undercooled liquid region before crystallisation. Depending on their composition, the formation of metastable intermediate phases, such as a quasicrystalline phase is possible. Due to the combination of early and late transition metals (ETM/LTM), these alloys are very interesting regarding their interaction with hydrogen. Amorphous Zr₅₅Cu₃₀Al₁₀Ni₅, Zr₆₅Cu_{17.5}Al_{7.5}Ni₁₀ and Zr₅₉Ti₃Cu₂₀Al₁₀Ni₈ ribbons were prepared by melt spinning. Their microstructure and thermal behaviour was checked by X-ray diffraction (XRD), transmission electron microscopy (TEM) and differential scanning calorimetry (DSC). The cathodic reactivity in 0.1 M NaOH of alloy samples at different microstructural states and after pre-etching in 0.1% HF was investigated applying potentiodynamic polarisation techniques. Hydrogen charging was performed galvanostatically at $i = -1$ to 20 mA/cm^2 . Hydrogenated samples were characterised by XRD, DSC, TEM and thermal desorption analysis (TDA). Electrochemical measurements on amorphous Zr₅₉Ti₃Cu₂₀Al₁₀Ni₈ samples revealed an increase in capacity by two orders of magnitude after pre-etching. Furthermore, compared to the corresponding crystalline alloy counterpart, the cathodic hydrogen reduction takes place at significantly lower overpotentials. At room temperature, the Zr-based alloys can absorb hydrogen up to $H/M=1.65$ while keeping the amorphous structure. Already small amounts of hydrogen cause a significant decrease of the thermal stability, i.e. a reduction of the supercooled liquid region, and a complete change in the crystallisation sequence. The hydrogen desorption is a two-stage process: ($T < 623 \text{ K}$) hydrogen desorption from high interstitial-site energy levels and ($T > 623 \text{ K}$) zirconium hydride formation and subsequent transformation under effusion of hydrogen. Hydrogen was found to suppress the oxygen-triggered formation of metastable phases upon heating and to support a primary copper segregation. At very high H/M ratios, severe zirconium hydride formation causes an enrichment of Cu, Ni and Al in the residual amorphous phase resulting in the crystallization of new stable intermetallic compounds.

HYDROGEN STORAGE IN ZR-CU-NI-AL-TI BULK METALLIC GLASSES

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The behavior of hydrogen in amorphous metal alloys has been studied for more than two decades. It was shown by many authors that hydrogen dissolved in amorphous metal could give rise to special features mostly unknown for the crystalline state. Some Ni-Zr and Mg-Ni based metallic glasses, mostly produced by melt-spinning or mechanical alloying, were found to have impressive capability in storing hydrogen. Metal hydride electrodes made up of amorphous metals also gave a very good electrochemical discharge capacity and cycle life. With the recent advances on the understanding and manufacturing of bulk metallic glasses (BMG), they have received considerable attention because of their superior properties such as strength, superplasticity and corrosion resistance. In this work the hydrogen storage capability of a Zr-based BMG (Zr-17.9Cu-14.6Ni-10Al-5Ti) has been studied. Crystalline samples were also included in the study for comparison. Differential scanning calorimetry and X-ray were used to examine the crystallization temperature and microstructures of these samples. A semi-automatic Sievert's type apparatus was used to measure the hydrogen absorption and desorption reaction of the metallic glass. The pressure-composition-isotherm measurement was performed in the range of 0.01 to 20 atm. Before the absorption test both the crystalline alloy and BMG samples were subjected to an activation process in vacuum at 150°C. It was found that the BMG could absorb an exceptionally high amount of hydrogen. For example, the hydrogen absorbed (H/M ratio) at room temperature, under 20 atm of hydrogen, was roughly between 3 to 5, which was about three times that absorbed in the crystalline samples. However, there were marked irregularities in the hydrogen desorption rate with respect to external pressure. That is, the amount of hydrogen desorpted was deviated from that predicted from Sievert's law, and no plateau was observed in the PCI curve as was in the crystalline alloy. This may be attributed to the very low diffusivity of hydrogen in BMG, or the nature of hydrogen traps in our BMG samples (i.e. a spectrum of traps vs. hydride in crystalline alloys). The hydrogen absorption/desorption cycle life for the BMG was longer than that of crystalline alloy. All these features strongly indicate the high potential for this Zr-based bulk amorphous alloy to be an effective hydrogen storage material. The crystallizing temperature was also dependent on the amount of hydrogen in the sample.

RESEARCH ON APPLICATION PROPERTIES OF Zr-BASED BULK AMORPHOUS ALLOYS

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Bulk Nd-Al-Fe-Co glassy alloys with diameter up to 5 mm were investigated by magnetic measurements, magnetic force microscopy (MFM) and high resolution electron microscopy (HREM) at room temperature. The results from the measurement of vibrating sample magnetometer show that these samples with compositions $\text{Nd}_{65}\text{Al}_{10}\text{Fe}_{25-x}\text{Co}_x$ ($x=0\sim 10\text{at.}\%$) and $\text{Nd}_{60}\text{Al}_{10}\text{Fe}_{20}\text{Co}_{10}$ display hard-magnetic properties with HC of ~ 300 kAm⁻¹, MS of ~ 10 Am² kg⁻¹, and Mr of ~ 7 Am² kg⁻¹. The MFM measurements of the $\text{Nd}_{60}\text{Al}_{10}\text{Fe}_{20}\text{Co}_{10}$ BMG show the existence of magnetic domains with a period of about 360 nm, and the clusters with the size up to 5 nm were observed by the HREM on the sample, but no such large-size clusters in melt-spun amorphous ribbon were revealed by HREM observation. The domain structure or cluster is believed to be associated with the appearance of hard-magnetic properties in this alloy system. The existence of the large-scale domains demonstrates that magnetic moment resulting from a great deal of short-scale ordered atomic clusters in the BMG has been aligned by exchange coupling.