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Tuning the Curie temperature of $Fe_{90}Sc_{10}$ nanoglasses by varying the volume fraction and the composition of the interfaces

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ABSTRACT

$Fe_{90}Sc_{10}$ nanoglass was produced by consolidating $Fe_{90}Sc_{10}$ glassy nanoparticles (GNp) into bulk solid material. The average diameters of the GNp, which were produced by inert gas condensation, decreased as He pressure decreased. The volume fraction of the interfaces within the nanoglass increased as the diameters of the primary GNp decreased. The segregation of the Fe atoms at the surfaces of the GNp varied, so the composition of the interfaces was different. As the Curie temperature of $Fe_{90}Sc_{10}$ nanoglass is primarily dependent on the volume fraction and the composition of the interfaces, the Curie temperature increased as He pressure decreased.

Nanoglasses are a new class of amorphous solid materials that are normally produced by consolidation of glassy nanoparticles (GNp). The knowledge surrounding nanoglasses show that the nanoglasses consist of glassy cores connected by interfaces of reduced density [1,2]. In addition, the composition and the short range order of the interfaces are different from the cores [3–5].

The interfaces cause the nanoglasses to exhibit several distinctive properties, setting them apart from the corresponding melt-spun ribbons with identical average compositions [1,2,6–8]. Witte et al. reported that $Fe_{90}Sc_{10}$ nanoglass is ferromagnetic at room temperature, while $Fe_{90}Sc_{10}$ melt-spun ribbon is paramagnetic [6]. They claimed that the enhanced ferromagnetism of $Fe_{90}Sc_{10}$ nanoglass is caused by interfaces with low atomic packing density. Therefore, the initial objective of the present study was to vary the diameters of the primary GNp, which will change the volume fraction of the interfaces, allowing the Curie temperature of the $Fe_{90}Sc_{10}$ nanoglasses to change.

The $Fe_{90}Sc_{10}$ GNp were produced by inert gas condensation (IGC) as described elsewhere [1]. The IGC chamber was backfilled with high purity He (99.9999%) at various pressures (0.2, 1, and 20 mbar) after evacuating to 4×10^{-8} mbar to produce GNp of various average diameters. The Fe—Sc alloys, with a composition of $Fe_{85.5}Sc_{14.5}$, were loaded into the temperature-controlled tungsten boats to evaporate the $Fe_{90}Sc_{10}$ GNp at the similar temperature. Disk-like $Fe_{90}Sc_{10}$ nanoglass pellets were produced by in situ consolidation of the GNp at 2 GPa and further by ex situ consolidation at 6 GPa.

The GNp were collected from the cold finger of the IGC system after the chamber was opened. Tiny GNp were diffused in acetone, ultrasonic vibrated for 2 min, and then the acetone was dropped onto carbon film that was supported by the transmission electron microscopy (TEM) grids. A Tecnai electron microscope was operated in the TEM mode at an accelerating voltage of 200 kV to obtain the GNp TEM images.

The amorphous state of the $Fe_{90}Sc_{10}$ nanoglasses was confirmed by X-ray diffraction (XRD) with a molybdenum source. The average composition of the $Fe_{90}Sc_{10}$ nanoglasses was confirmed by electron diffraction X-ray (EDX). Superconducting Quantum Interference Device (SQUID) magnetometry and Mössbauer spectroscopy were applied to characterize the magnetic properties of the samples. The specimens for the Atom Probe Tomography (APT) characterization were cut from the nanoglass pellets via a focused ion beam (FIB). The Local Electrode Atom Probe was operated in the laser pulsing mode to obtain the elemental distribution of the nanoglasses.

The average diameters of the GNp were counted from the TEM images using Image J software (National Institutes of Health, USA). The GNp that were produced in 20 mbar He (20 mbar GNp) had an average diameter of approximately 12 nm. The average diameter of the 1 mbar GNp was about 8 nm, but the average diameter of the 0.2 mbar GNp was difficult to count due to heavy aggregation of the GNp. According to Granqvist [9], the average diameters of the nanoparticles decrease as inert gas pressure decreases, so the average diameter of the

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0.2 mbar GNp should be the smallest. This is consistent with the aggregation behavior of the nanoparticles. The total surface energy of nanoparticles increases when the diameter decreases, so in order to decrease energy, the nanoparticles prefer to aggregate to decrease the total surface area. Therefore, the average diameter of the 0.2 mbar GNp should be the smallest, and the volume fraction of the interfaces within the corresponding nanoglass should be the highest.

The magnetization (M) versus the temperature (T) curves of the $Fe_{90}Sc_{10}$ nanoglasses are shown in Fig. 1a. As the Curie temperature could be approximately estimated from the maximum of the dM/dT curves based on the slopes of the curves, the Curie temperature increased as the volume fraction of the interfaces increased. The magnetization (M) versus the external field (H) curves confirmed the variations in the Curie temperature of the samples. As shown in Fig. 1b, the 0.2 mbar and 1 mbar nanoglasses were ferromagnetic at room temperature, while the 20 mbar nanoglass was paramagnetic. The 0.2 mbar nanoglass was more saturated than the 1 mbar nanoglass, indicating that the Curie temperature of the 0.2 mbar nanoglass was the highest.

Mössbauer spectroscopy is a powerful tool to characterize local magnetic properties of materials, and it has been applied to demonstrate the existence of ferromagnetic interfaces of $Fe_{90}Sc_{10}$ nanoglasses [6,10]. Fig. 2 presents the magnetic spectra of the $Fe_{90}Sc_{10}$ nanoglasses at room temperature. The original spectrum of the 1 mbar nanoglass (Fig. 2b) was fitted with two sub-spectrums, which corresponded to the two components of the $Fe_{90}Sc_{10}$ nanoglass previously reported by Witte et al. [6] The single curve represents the magnetic disordered component, while the sextet represents the magnetic ordered component. Normally, the area fraction of the sub-spectrum is proportional to the relative percentage of the Fe atoms. The area fraction of the sextet was larger than the relative percentage of Fe atoms located in the interfaces within the $Fe_{90}Sc_{10}$ nanoglass at room temperature, as the magnetic order in the interfaces extended inwards (to the cores) due to exchange interactions [6]. Thus, the interfaces and some outer-layers (near-interface) of the cores were magnetically ordered at room temperature.

As the average diameters of the primary GNp decreased, the volume fraction of the interfaces increased. When the diameter of the GNp decreased to some value, the entire core was ferromagnetic, due to the enhanced exchange interactions. This caused the single line that represented the magnetic disordered component to disappear in the 0.2 mbar Mössbauer spectrum (Fig. 2c). The hyperfine field curve (the inserted) indicated that two components with different electronic structure existed. The lower magnetic field belonged to the cores and the higher magnetic field was attributed to the interfaces.

As shown in Fig. 2a, the disappearance of the sextet suggests that the interfaces within the 20 mbar nanoglass were paramagnetic, or the interfaces were ferromagnetic but the volume fraction was too small to be detected. Assuming the thickness of the interfaces within the nanoglass is a constant d, then the volume fraction of the interfaces (F) is estimated as [11]:

$$F = 3d/D \tag{1}$$

where D is the average diameter of the GNp. The 20 mbar GNp has a D value of approximately 12 nm, meaning $F_{(d=12\ nm)} = 83\% F_{(d=10\ nm)}$. The relative area fraction of the interfacial sub-spectrum at 10 K was 35% for the nanoglass that was produced by consolidation of the 10 nm sized GNp, indicating that the Fe percentage of the interfaces was 35% [6]. Assuming that the density and Fe concentration of the interfaces remained constant, the Fe percentage of the interfaces within the 20 mbar nanoglass was estimated to be: $35\% \times 83\% = 29\%$. If the density-reduced interfaces within the 20 mbar nanoglass were ferromagnetic, this percentage of Fe atoms located in the interfaces should be detected by Mössbauer spectroscopy via a sextet-like spectrum. The sextet disappeared, indicating that the interfacial area of the 20 mbar nanoglass was paramagnetic, and its Curie temperature was the lowest. Since the Curie temperature of the Fe—Sc glasses was related to the Fe concentration [12] and $Fe_{90}Sc_{10}$ nanoglasses are chemically heterogeneous with Fe enriched interfaces [3], it was deduced that the Curie temperature of the interfaces within the 20 mbar nanoglass was related to the Fe concentration of the interfaces.

Atom Probe Tomography was applied to the 1 mbar $Fe_{90}Sc_{10}$ nanoglass to confirm the chemically heterogeneous structure of the nanoglass. As shown in Fig. 3, the Fe concentration profiles of the Fe and the Sc fluctuated like waves, suggesting that the 1 mbar $Fe_{90}Sc_{10}$ nanoglass was chemically heterogeneous. Fe content fluctuated from about 86 at.% to 91 at.% with variation in the range of 5 at.%. The average Fe concentration of the FIB sample was 88.5%. The crests of the small humps (as indicated by the red arrows) in the red waves might correspond to the interfaces with a higher Fe concentration, and the distance between the crests of the nearest two humps might be approximately equal to the diameter of a compacted glassy nanoparticle.

For the nanoparticles with composition $A_X B_{1-X}$, the relationship between the surface composition (X^S) and the core composition (X^C) may be determined as [13,14]:

$$\frac{X^S}{X^C} = \frac{exp\left(\frac{Q_{Seg}}{RT}\right)}{1 + X^C\left[exp\left(\frac{Q_{Seg}}{RT}\right) - 1\right]} \tag{2}$$

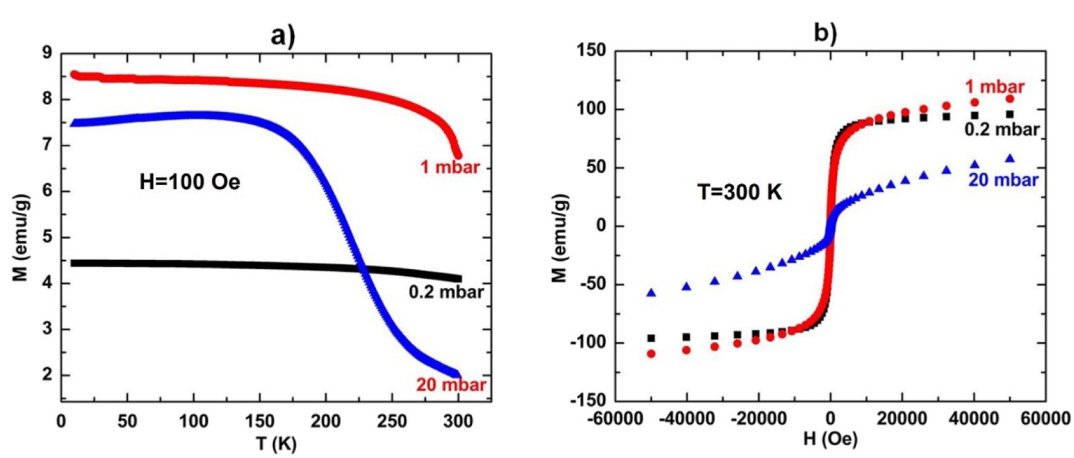

Fig. 1. The magnetization versus the temperature curves at 100 Oe (a), and the magnetization versus the external field curves at 300 K(b) for the nanoglasses. The nanoglasses were produced by consolidation of primary GNp with various average diameters. As the diameters of the GNp decreased, the Curie temperature of the corresponding nanoglass increased.