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The Magnetic and Mechanical Hardness of the Intermetallic Compounds $SmCo_5$ and $LaCo_5$

R. A. McCURRIE, G. P. CARSWELL
School of Materials Science, The University of Bradford, Bradford 7 UK

J. B. O'NEILL
Rolls Royce and Associates Ltd, Derby, UK

The magnetisation, coercivity, H_C, and remanence coercivity, H_R, have been measured for the intermetallic compounds $SmCo_5$ and $LaCo_5$. The coercivities H_C and H_R for $SmCo_5$ are very much greater than those for $LaCo_5$. The differences in these parameters are much greater than would be expected from a simple theoretical model, so that they cannot be accounted for in terms of differences in the magnetocrystalline anisotropy constants. Since the specimens used for the magnetic measurements were produced by mechanical comminution, Knoop hardness measurements were made in an attempt to account for the magnetic behaviour in terms of the crystallographic damage and plastic deformation produced during the grinding process. The hardness results show that, within experimental error, the $SmCo_5$ is very nearly isotropic, whereas the $LaCo_5$ is very anisotropic on the $\{10\bar{1}0\}$ planes with a Knoop hardness of 138 in the $\langle 0001 \rangle$ directions and 511 in the $\langle 12\bar{1}0 \rangle$. It is concluded that plastic deformation will occur more easily in $LaCo_5$ and that this could, to some extent, explain the comparatively low coercivities.

1. Introduction

It is now well known that the hexagonal lanthanide-cobalt intermetallic compounds, LCo_5, with the $CaCu_5$ structure (fig. 1) [1-9] possess exceptional magnetic hardness. Coercivities $\sim$ 5000 to 15000 Oe or more can be obtained relatively easily by grinding in air to particle sizes < 20 μm and subsequently aligning the particles in paraffin wax by a field of $\sim$ 20000 Oe. These extremely high coercivities have been attributed to the enormous uniaxial magnetocrystalline anisotropy field $\sim$ 300 kOe for $SmCo_5$ [10, 11] but a detailed theory of the mechanism of magnetisation reversal has yet to be presented. Owing to the extremely high anisotropy fields (i.e. the fields required to saturate the materials in directions perpendicular to the easy [0001] direction, given by $H_A = 2K_1/M_S$ where K_1 is the uniaxial magnetocrystalline anisotropy constant and M_S is the saturation magnetisation in emu/cm³) it seems most unlikely that coherent rotational processes would be important. Becker [12] and Westendorp [6] have therefore suggested that wall nucleation and pinning processes are operative.

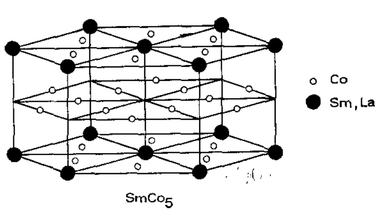

Figure 1 $CaCu_5$ structure.

2. Magnetic and Mechanical Properties

The contrasting magnetic behaviour of $SmCo_5$ and $LaCo_5$ is illustrated in figs. 2 and 3. The methods of specimen preparation were identical, but it is clear from fig. 2 that aligned assemblies of $SmCo_5$ give very much higher coercivities than $LaCo_5$. This difference could to some extent be explained by the fact that the anisotropy field for $SmCo_5$ is $\sim$ 300 kOe while that for $LaCo_5$ is $\sim$ 175 kOe. A further important point is that the

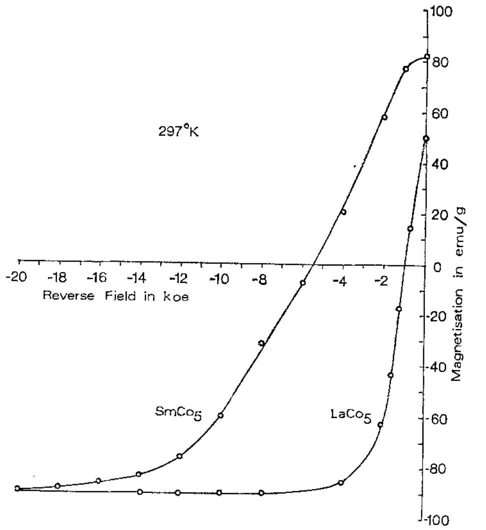

Figure 2 Demagnetisation curves for $SmCo_5$ and $LaCo_5$.

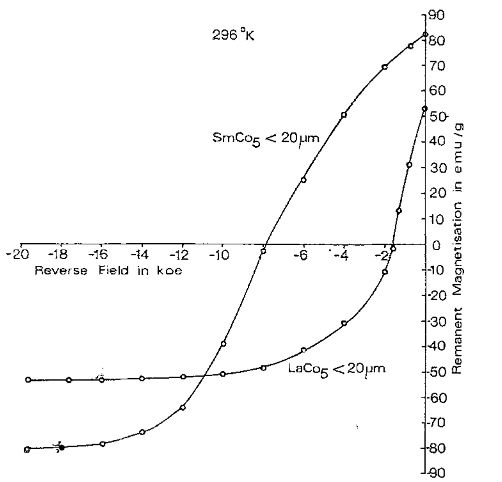

Figure 3 Demagnetising remanence curves for $SmCo_5$ and $LaCo_5$.

shape of the coercivity distribution curves (fig. 4) are quite different. These were determined from the demagnetising remanence curves (fig. 3) using the method given by McCurrie [7]. In the case of $SmCo_5$ the skewness of the distribution of intrinsic coercivities is comparatively small and the modal value is very close to the measured or macroscopic remanence coercivity, H_R (7800 Oe). However, the $LaCo_5$ particles have a positively skew distribution, i.e. there are many more particles with low intrinsic coercivities, although there are particles with intrinsic coercivities as high as 20000 Oe. If it can be assumed that the

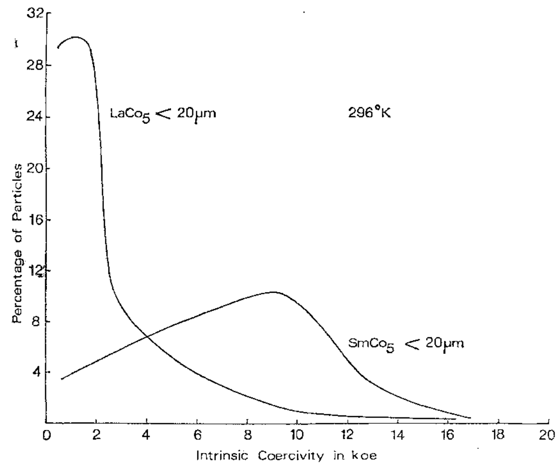

Figure 4 Intrinsic coercivity distribution curves for $SmCo_5$ and $LaCo_5$.

$SmCo_5$ and the $LaCo_5$ specimens have similar distributions of particle sizes, then it may be that the differences in the magnetic behaviour can, to some extent, be accounted for in terms of the crystallographic damage produced by the grinding and sieving processes.

So far, little attention has been given to the fact that the intermetallic compounds in the series $SmCo_5$, $LaCo_5$, $CeCo_5$, $PrCo_5$ and YCo_5 are all extremely hard and brittle at room temperature. Their extreme resistance to plastic deformation can be illustrated by the fact that well defined equilibrium domain structures have been observed by McCurrie and Carswell [8] on mechanically polished specimens. This suggests that the polished surfaces were relatively free of plastic deformation. Attempts to observe equilibrium domain structures on plastically deformed surfaces such as mechanically polished alloys of Si-Fe usually give rise to the well-known maze patterns [13]. The mechanical hardness of the materials is therefore of considerable interest with regard to the interpretation of the extremely high coercivities.

It is now well established that the coercivities of most magnetic materials increase as the particle size decreases [14-16]. This has also been observed for $SmCo_5$ [9, 12]. This increase in coercivity has usually been attributed to the presence of single domain particles in which magnetisation reversal takes place by coherent rotation of the magnetisation vector. The coercivities are therefore expected to be $\sim 2K_1/M_S$ in the usual notation. Using the simple argument suggested by Kittel [17] for materials with high uniaxial anisotropy, McCurrie and Carswell [9] have shown that the critical radius for single domain behaviour is about 4 μm. It has been observed that particles with diameters as high as 40 μm give coercivities $\sim$2000 Oe. It appears, therefore, that magnetisation reversal must occur by (a) nucleation and movement of 180° domain walls, (b) some other incoherent mechanism or (c) a combination of (a) and (b). Thus, in order to avoid easy nucleation of reverse domains, resulting in low coercivities, the retention of a high uniaxial magnetocrystalline anisotropy after grinding is essential. Aharoni [18, 19] has shown that the presence of imperfections can lead to local reductions in K_1 and hence easier nucleation of reverse domains, but the theoretical estimates are still very much higher than the experimental values. However, it is perhaps still reasonable to expect that the absence of regions of plastically deformed material and stacking faults will be conducive to higher coercivities. It is also possible that internal magnetostatic charges corresponding to div $M_s \neq 0$ could be produced by stacking faults, mechanical slip, dislocations or microcracks. The reduction of the magnetostatic energy associated with these crystallographic imperfections could result from the formation of a closure domain structure of some kind. Although the imperfections will act as domain wall pinning centres and so tend to increase the coercivity, this effect would be far outweighed by the fact that magnetisation reversal is very much easier once the reverse domains have been nucleated.

The purpose of the present paper is to investigate the mechanical hardness of $SmCo_5$ and $LaCo_5$ in an attempt to account for the observed differences in the magnetic hardness.

3. Knoop Hardness Measurements

Investigation of the mechanical properties using the Knoop hardness indenter [20] has a number of advantages over other indenters, particularly for brittle materials. The Knoop indenter has an asymmetric shape which provides the following advantages: (a) measurable indentations can be obtained using relatively light loads (15 to 50 g), thus enabling small grains or crystallites to be used in the investigation; (b) the apex of the indenter penetrates the surface to a lesser depth than the Vickers indenter – the latter develops higher stresses which tend to crack brittle materials; (c) the elastic recovery takes place largely in the transverse direction on removal of the load, so that the measured indentation diameter is much closer to the unrecovered value; and (d) the anisotropy of the mechanical properties can be measured.

4. Experimental Results

In general, cast specimens of the lanthanide-cobalt intermetallic compounds have very small grain sizes so that the accurate determination of their orientations by the conventional Laue technique is very difficult and time consuming. McCurrie and Carswell [8] have suggested that careful interpretation of the magnetic domain structures within a grain enables a good approximation of its orientation to be obtained. An (0001) surface will almost certainly be that on which the most finely divided domain structures appear. These usually consist of closely spaced undulating or zig-zag 180° domain walls. The extremely high magnetocrystalline anisotropy energy will almost certainly prevent the formation of closure domain structures, so that the magnetostatic energy associated with div $M_s \neq 0$ on the surface will be reduced by the formation of reverse spike domains. Grains with orientations very close to the prismatic $\{10\bar{1}0\}$ planes are characterised by simple domain structures with widely spaced 180° domain walls parallel to the [0001] easy direction of magnetisation. Examples of the domain structures on both (0001) and $\{10\bar{1}0\}$ planes are shown in fig. 5. Other examples are given by McCurrie and Carswell [8].

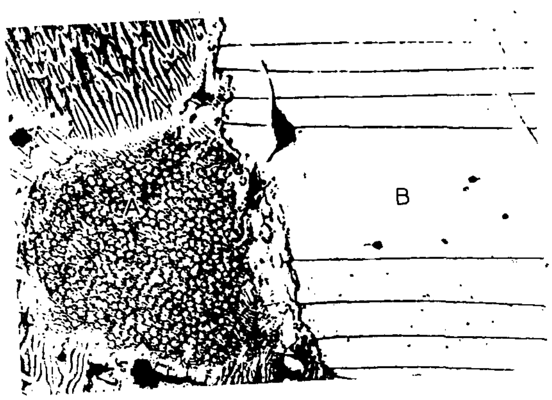

Figure 5 Domain structures on basal (A) and prismatic (B) planes on $LaCo_5$ ($\times$ 316).

The hardness measurements were made with a Leitz Durimet Tester with a diamond Knoop indenter. The specimens were prepared by mechanical polishing down to 1 μm diamond paste. They were then thoroughly washed in water and methyl alcohol and subsequently dried in a stream of warm air. A small drop of colloidal magnetite was then placed on the specimen surface and allowed to dry. The resulting domain structures were then used to select grains with particular orientations for indentation. After full application of the load (200 g), the indenter was left in contact with the specimen surface for 10 sec before removal of the load. Five grains having an (0001) surface, and five having a $\{10\bar{1}0\}$ surface were selected for hardness measurement. Indentations on the $\{10\bar{1}0\}$ planes were made in the $\langle 0001 \rangle$ and $\langle 1\bar{2}10 \rangle$ directions as estimated from the domain wall structures within the grain. Indentations were also made at 90° to each other on the (0001) plane; ideally these would have been in $\langle 1\bar{2}10 \rangle$ and $\langle 10\bar{1}0 \rangle$ type directions, but it was not possible to orientate the (0001) domain patterns. The hardness results for $SmCo_5$ and $LaCo_5$ are summarised in tables I and II.

TABLE I Knoop Hardness Numbers – $SmCo_5$

	Basal plane {0001}		$\{10\bar{1}0\}$ plane	
	(*a*)	⊥ *to* (*a*)	$\langle 0001 \rangle$	$\langle 1\bar{2}10 \rangle$
	580.8	643.6	643.6	613.7
	575.9	641.6	582.5	659.3
	637.8	596.0	590.0	566.2
	615.5	665.4	611.9	671.5
	569.4	619.1	641.6	585.8
Mean	596	633	614	619

TABLE II Knoop Hardness Numbers – $LaCo_5$

	Basal plane {0001}		$\{10\bar{1}0\}$ plane	
	(*a*)	⊥ *to* (*a*)	$\langle 0001 \rangle$	$\langle 1\bar{2}10 \rangle$
	534.1	532.6	156.6	548.1
	544.5	532.6	135.5	505.1
	541.5	539.1	126.3	445.8
	550.5	535.5	134.4	505.1
	523.1	515.5	138.0	550.1
Mean	539	531	138	511

5. Discussion and Interpretation of Results

The most interesting result obtained from the present investigation is that $LaCo_5$, unlike $SmCo_5$, exhibits a marked hardness anisotropy on the $\{10\bar{1}0\}$ planes.

Daniels and Dunn [21] suggested that hardness anisotropy in single crystals is controlled by bulk plastic flow on the operative slip systems of the material. They argued that the deforming force imposed by the individual facets of the indenter can be resolved into the slip directions on the slip planes. The magnitude of this resolved shear stress acting on mobile dislocations on the slip planes is then a measure of the ease with which plastic deformation can occur. These stresses vary in magnitude for different orientations of the indenter on a given plane; the higher the stresses, the softer the crystal will appear to be.

In general, there are two slip systems which can operate in hexagonal materials – the {0001} $\langle 11\bar{2}0 \rangle$ and the $\{10\bar{1}0\}\langle 1\bar{2}10 \rangle$. Brookes *et al* [22] showed that the hardness anisotropy, i.e. direction of maximum hardness, depends on which of these two slip systems is operative. For crystals deforming on the $\{0001\}\langle 11\bar{2}0 \rangle$ system, the direction of maximum hardness on the $\{10\bar{1}0\}$ plane is the $\langle 0001 \rangle$ direction, whereas crystals with the $\{10\bar{1}0\}\langle 1\bar{2}10 \rangle$ have a maximum hardness in the $\langle 1\bar{2}10 \rangle$ directions. They also predict that there will be little or no Knoop hardness anisotropy on the (0001) plane for either slip system. The system which operates in a given material depends to some extent on whether the *c*/*a* ratio is greater, or less than, the critical value of 1.63 for close packing of spheres. Since the c/a ratios for $SmCo_5$ and $LaCo_5$ are 0.7991 and 0.7777 respectively the operative slip system is expected to be $\{10\bar{1}0\}$ $\langle 1\bar{2}10 \rangle$. This is confirmed experimentally in the case of $LaCo_5$.

The Knoop hardness values for $LaCo_5$ are anisotropic and of the type which suggests prismatic slip. It is therefore reasonable to assume that dislocations are able to move and multiply easily on this slip system. In $SmCo_5$, however, the apparent absence of any hardness anisotropy could imply either (a) that although the dislocations move on the prismatic planes, they are not able to multiply to any great extent, or (b) that $SmCo_5$ slips on the basal plane. Attempts to observe the dislocations directly using electron and optical microscopy have been unsuccessful so that no conclusive evidence is available.

The apparent difference in the dislocation mechanics of the two alloys could therefore be an important factor in accounting for the differences in the magnetic hardness. If the dislocations are more free to move and multiply in $LaCo_5$ then, as a result of the grinding process, there will be more defects per unit volume which could act as nucleation sites for reverse domains.

By annealing freshly ground $SmCo_5$ powder at

1080° C for about 30 min Westendorp [6] obtained coercivities ~ 35000 Oe. This suggests that the effect of the annealing process is to repair the crystallographic damage produced by the grinding and sieving processes.

The effect of grinding at low temperatures and subsequent annealing at high temperatures is currently being investigated for both $SmCo_5$ and $LaCo_5$.

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