Iron Oxide-Metal Composites via Mechanical Milling

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Abstract: Study investigates the dynamic dissolution of iron oxides in various metals (Fe, Ni, Cr, Zr, Ti, and Al) under high-pressure compression shear at 300K, followed by thermal annealing. Advanced characterization techniques, including Mossbauer spectroscopy, X-ray diffraction analysis, and transmission electron microscopy, were employed to analyze the dissolution and precipitation processes. The results reveal that the formation of secondary oxides and nanocrystalline structures depends on the ability of metals to form solid solutions and chemical compounds with iron and oxygen. The findings demonstrate the possibility of deformation-induced oxygen transport and the formation of specialized oxides suitable for oxide dispersion-strengthening.

Keywords: metal, mechinical, X-ray iron

1. Introduction

Over the past 25 years, mechanical synthesis has emerged as a prominent method for producing novel materials, particularly dispersion-strengthened systems. This technique involves mechanical alloying of powders in ball mills, enabling the creation of unique material properties. However, traditional methods face challenges in controlling treatment conditions and composition [1]. In contrast, the mechanical synthesis under compression shear (CS) method offers precise control over alloy composition, temperature, and deformation rate [2]. This study explores the CS method for preparing oxide dispersion-strengthened (ODS) alloys, focusing on the dynamic dissolution of iron oxides and the formation of secondary oxides during subsequent annealing. By examining the influence of matrix properties on these processes, this research aims to advance the understanding of mechanical synthesis and its applications in creating innovative materials [3].

The potential of mechanical synthesis under compression shear to produce oxide dispersion-strengthened (ODS) alloys with tailored properties. By investigating the dynamic dissolution of iron oxides and the subsequent formation of secondary oxides, this study sheds light on the underlying mechanisms and kinetics of these processes. The findings of this research are expected to provide valuable insights into the development of novel ODS alloys with enhanced performance, contributing to advancements in various fields such as aerospace, energy, and transportation. Ultimately, this study aims to expand the understanding of mechanical synthesis and its capabilities in creating innovative materials with unique properties [4].

This research has significant implications for the design and development of new materials with improved mechanical properties, such as strength, toughness, and resistance to corrosion and high-temperature degradation. By elucidating the role of metal matrices in the deformation-induced dissolution of iron oxides and the formation of secondary oxides, this study can inform the optimization of processing conditions and composition to achieve desired material properties. Additionally, the findings of this research can be applied to the development of novel processing routes for the production of advanced materials, enabling the creation of innovative products and technologies. Ultimately, this study contributes to the advancement of materials science and engineering, with far-reaching impacts on various industries and applications [5].

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2. Material and Procedure

The study involved selecting metal matrices based on their varying abilities to form metal solid solutions with iron and oxygen from initial oxides. The metals chosen included iron, nickel, chromium, titanium, zirconium, and aluminum, selected for their differing oxidizability. Specially prepared ^{56}Fe, with a certified low content of resonance ^{57}Fe (<0.2%), was used for the iron matrix to trace iron atom transfers during phase transformations. Nickel and chromium were chosen for their ability to form continuous solid solutions with iron, whereas titanium, zirconium, and aluminum were selected for their tendency to form intermetallic compounds with iron. Mechanical alloying and activation processes were conducted using the CS method in ball mills, and solid solutions were formed in the Ti-Fe, Zr-Fe, and Al-Fe systems, showing different iron solubility levels depending on the metal matrix used.

Standard hematite (β-Fe_2O_3) and synthesized magnetite (Fe_3-yO_4) powders served as the oxide components. The magnetite was produced by mechanically activating hematite followed by annealing at 1075 K, resulting in a nonstoichiometric spinel structure. The oxides were mixed with metal powders obtained by filing bulky metal samples, with the mixtures containing 60% metal and 40% oxide by mass. Filing produced coarse powders with an average particle size of about 200 μm, which were then separated by size using a screening machine.

The mixture underwent intensive deformation through compression shear at 6–8 GPa in Bridgman anvils, which were made of sintered WC carbide. This process was conducted at room temperature (25°C) with a rotation speed of approximately 1 rpm and involved 5–10 revolutions, corresponding to a true deformation of $\epsilon = 7\tilde{}8$. During this process, radial flow of the sample material was observed initially, followed by stabilization of the sample's thickness as torsional deformation continued. The treated sample, a metallic disk of 5–6 mm thickness and approximately 80 μm in diameter, was further thinned to 30 μm from both sides.

The synthesized CS samples were annealed under vacuum at 690 and 970 K for 30 minutes to allow the formation of secondary oxides. The choice of annealing conditions was based on the metal matrices' abilities to form these oxides. The samples were analyzed using Mössbauer spectroscopy, electron microscopy, and X-ray diffraction. Mössbauer spectra were recorded using 14.4 keV gamma-quanta from a ^{57}Co(Cr) source, and the data was processed with MS Tools software to reconstruct the density function of the centers of gravity of the resonance absorption lines. The spectra were then modeled as a combination of modified Gaussian lines, which allowed for the identification of different iron positions in oxides and alloys.

The microstructure of the samples was examined using a JEM-200CX transmission electron microscope, and the X-ray diffraction analysis was conducted with Cu radiation to characterize the crystalline structure. These techniques provided detailed insights into the phase composition and structural changes occurring during mechanical synthesis and annealing processes.

3. Results

The text describes a study on the decomposition of hematite and magnetite in a mixture with metal matrices. The results show that the decomposition is intensified at their deformation in a mixture with metal matrices. The study used Mössbauer spectroscopy to analyze the phase composition and structural changes during the synthesis process.

The transformation formula for the decomposition of hematite is given as:

$$\mathrm{Me} + \beta\text{-}\mathrm{Fe_2O_3} \rightarrow \mathrm{Fe}_{3-y}\mathrm{O}_4 + \mathrm{Fe}_{1-x}\mathrm{O} + \text{Fe-O} + \text{Me-Fe} + \text{Me-Fe-O} + \beta\text{-Fe-Me}$$

Where Me represents the metal matrix, β-Fe_2O_3 is hematite, $Fe_{3-y}O_4$ is magnetite, $Fe_{1-x}O$ is wustite, Fe-O is iron oxide, and β-Fe-Me is an intermetallic compound.

The study found that the decomposition process depends on the ability of the metal matrix to form secondary oxides. The formation of wustite and reduction of metal iron were observed during the synthesis process.

The Mössbauer spectra of the MS samples showed the presence of various phases, including deformation-induced oxides $Fe_{3-y}O_4$ and $Fe_{1-x}O$, and excess oxygen in the metal matrix. The spectra also showed the formation of new phases, such as Me-Fe-O and Fe-O, due to the reaction between the metal matrix and the oxides.

The study also found that annealing influences the ratio of phases in the MS samples with different metal matrices. The transition from deformation-induced oxides to stoichiometric magnetite was observed during annealing.

The X-ray diffraction patterns and electron microscopy examination confirmed the formation of a nanocrystalline structure in the MS alloys, with grain sizes ranging from 3-30 nm. The study suggests that the formation of secondary oxides and increase of the boundary surface strongly retarded the growth of nanograins during annealing.

Mathematical expressions used in the text include:

- Integral intensities ($S, \%$) of the subspectra of structural and phase components
- Mössbauer parameters, such as isomer shift and magnetic field
- Stoichiometry of the initial iron oxide and the reduced iron
- Concentration-inhomogeneous solid solutions, modeled as a superposition of single lines and doublets
- Ratio of phases in the MS samples, represented by the relative integral intensity of the sextets

4. Discussion

The discussion focuses on the intensification of the decomposition process of iron oxides in mixtures with metal matrices, driven by deformation-induced dissolution of oxides into the metals and the subsequent formation of solid solutions [6]. This phenomenon is explained through various factors, including the role of vacancies, interstitial atoms, and the refining of the structure that occurs during cold deformation.

4.1. Deformation-Induced Dissolution and Phase Transformations

The primary mechanism for the observed intensification of iron oxide decomposition involves deformation-induced dissolution. The formation of solid solutions is facilitated by the introduction of vacancies and interstitial atoms during cold deformation, which enhances the transport of iron and oxygen atoms from the oxides to the surrounding metal matrix [7]. This process can be summarized as a sequence of phase transformations, particularly for hematite (β-Fe_2O_3):

$$\beta\text{-Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4 \rightarrow \text{FeO}$$

4.2. Formation of Secondary Phases

In alloys with matrices such as Zr, Ti, Cr, or Al, Mössbauer spectroscopy, X-ray diffraction, and TEM analyses reveal the formation of additional quantities of β-Fe and secondary oxides during annealing [8]. This phenomenon is attributed to the decomposition and redox reactions in the nonequilibrium solid solutions formed during deformation. The primary factors influencing the phase composition during annealing include the matrix metals' ability to dynamically dissolve oxide elements and their inherent oxidability.

4.3. Redox Reactions and Dynamic Solubility

The discussion highlights the dynamic solubility of oxygen in matrix metals like titanium and zirconium, which contributes to the decomposition of Me–Fe solid solutions and the formation of secondary oxides such as TiO_2 and ZrO_2. The relevant redox reactions can be described by the following equations:

$$Ti + 2Fe_2O_3 \rightarrow 4FeO + TiO_2$$

$$Zr + 2FeO \rightarrow 2Fe + ZrO_2$$

$$2Al + Fe_2O_3 \rightarrow 2Fe + Al_2O_3$$

These reactions demonstrate the significant role of the matrix metal's reactivity and solubility in determining the final phase composition.

4.4. Influence of Matrix Metals

The influence of different matrix metals on the decomposition process is further analyzed through the solubility and reactivity of these metals. For example, titanium has a high solubility for oxygen at room temperature, leading to a large quantity of reduced iron as β-Fe and the formation of Ti–Fe intermetallic compounds. On the other hand, aluminum shows minimal decomposition of hematite due to its low oxygen solubility, resulting in limited formation of secondary oxides [9].

4.5. Absence of Reduced Iron in Certain Matrices

In matrices such as Ni and Cr, the absence of additional quantities of reduced iron during annealing is explained by the equilibrium solubility of iron from the oxides into the matrix [10]. For instance, in a Ni matrix, the high solubility of iron leads to homogenization or decomposition processes during annealing, controlled by normal diffusion processes typical of binary solid solutions like Ni–Fe. The poor solubility of oxygen in nickel limits its involvement in phase transformations during heating.

4.6. Equilibrium Decomposition and Oxidation

The study also discusses the equilibrium decomposition and oxidation processes in the Me–Fe–O structure, particularly in conditions of high deformation-induced vacancy density. These processes can take place even at room temperature over a short period, as observed in earlier studies on the deformation dissolution of pearlite in high-carbon steel. The presence of β-Fe as a reduced product, preserved during annealing, indicates that it is the final product of phase transformations, resulting from the decomposition of deformation-induced nonequilibrium solid solutions [11].

4.7. Final Mechanism of Phase Transformations

Based on the results from Mössbauer, TEM, and X-ray diffraction analyses, the mechanism of phase transformations during annealing of mechanically synthesized CS samples is interpreted as the decomposition and redox reactions of oxygen-supersaturated Me–Fe–O solid solutions, along with dispersed iron oxides [12]. The intensity of these processes and the ratio of decomposition products are strongly influenced by the reactivity of the matrix metals, highlighting the complex interplay between dynamic solubility, redox reactions, and the structural characteristics of the materials involved.

5. Conclusion

This study demonstrates the significant role of deformation-induced processes in the decomposition of iron oxides when mixed with metal matrices. The primary mechanisms involve the dissolution of oxides into the metals, facilitated by the introduction of vacancies and interstitial atoms during cold deformation, which intensifies the transport of iron and oxygen atoms to the surrounding metal matrix.

Key findings include the observation that different metal matrices, such as Zr, Ti, Cr, and Al, significantly influence the decomposition process. The formation of additional quantities of β-Fe and secondary oxides, such as TiO_2 and ZrO_2, during annealing is attributed to the dynamic solubility of oxygen in these matrices and their oxidability. The study highlights the importance of redox reactions, with specific reactions such as:

$$Ti + 2Fe_2O_3 \rightarrow 4FeO + TiO_2,$$

$$Zr + 2FeO \rightarrow 2Fe + ZrO_2,$$

$$2Al + Fe_2O_3 \rightarrow 2Fe + Al_2O_3,$$

These findings suggest that the matrix metal's reactivity and solubility are critical in determining the final phase composition. In particular, the presence of β-Fe as the reduced product of phase transformations indicates its role as the final product resulting from the decomposition of deformation-induced nonequilibrium solid solutions.

The absence of additional reduced iron in matrices like Ni and Cr is linked to the high equilibrium solubility of iron in these metals, leading to homogenization during annealing. This study concludes that the mechanism of phase transformations during annealing of mechanically synthesized CS samples involves the decomposition and redox reactions of oxygen-supersaturated Me–Fe–O solid solutions. The intensity and product ratio of these processes depend heavily on the reactivity of the matrix metals, underscoring the complex interactions at play in these materials.

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