N84-33566 BMI-35145

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Report

SEVENTH QUARTERLY TECHNICAL PROGRESS REPORT
FOR THE PERIOD ENDING
August 10, 1984

on

THE INFLUENCE OF CONTAINERLESS UNDERCOOLING AND RAPID SOLID-STATE QUENCHING ON THE SUPERCONDUCTIVE AND MAGNETIC PROPERTIES OF SOME CLUSTERING ALLOY SYSTEMS

to

GEORGE C. MARSHALL SPACE FLIGHT CENTER
Alabama 35812

August 10, 1984

by

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CONTRACT NO. NAS8-35145
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1. GENERAL PURPOSE AND SCOPE

The proposed research has to do with the properties of clustering alloy systems and the manner in which they are influenced by rapid quenching from a containerless undercooled melt. It was postulated that rapid quenching under such conditions would result in highly disordered metastable alloys, and furthermore, that alloys in such conditions would possess physical properties characteristically different from those of alloys in the annealed equilibrium state. The scope of the program is essentially to gauge the influence of containerless undercooling on the submicrostructure of clustering-type alloys, using certain physical properties as diagnostic tools. Microstructures and macrostructures were to be examined using optical- and scanning-electron microscopy.

2. HISTORY

As indicated in the First Quarterly Report, it was decided to focus attention on Fe-Cr-Ni and related alloys; in particular, austenitic stainless steels. The alloys selected for initial study were:

AISI 310S (Fe-24.7Cr-20.4Ni)
AISI 316 (Fe-16.8Cr-11.7Ni)
Nitronic 40 (Fe-22.8Cr-6.5Ni-93Mn).

As indicated in the Second Quarterly Report (Third-Quarter Plan), it was intended to prepare samples in the annealed condition and also in the rapidly quenched condition in order to bracket the conditions expected of a drop-tube processed sample.

During the Third Quarterly Reporting Period some samples of the above-mentioned alloys were annealed according to 1h/1050 C/air cool; others were splat quenched through the courtesy of the Oak Ridge National Laboratory using the hammer-and-anvil method. Magnetization measurements were performed over the temperature range 4.2 to 298 K on each of the three samples, in both conditions, using the vibrating-sample magnetometer (six tests in all), and some data-analysis was carried out.

During the Fourth Quarterly Period further magnetic data-analysis was carried out. In addition, after the drop-tube at NASA was furnished with levitation-melting equipment some preliminary tests with it were conducted to determine the optimal sample size. The best sample for submission to NASA was determined to be a sphere weighing about 300 mg. Using wire samples in Battelle's electron-beam melting furnace, many samples conforming exactly to those specifications were prepared and sent to NASA for drop-tube processing. Some other samples were also prepared mechanically prior to submission to NASA.

During the Fifth Quarterly Period, drop-tube processed samples began to be received from NASA-Marshall (in particular, packages were received on November 11 and December 13, 1983). Since these were mostly ferromagnetic after processing, magnetization measurements were carried out only at room temperature. Some microstructures were observed using the scanning electron microscope and all of the samples were examined using conventional optical metallography. The ferromagnetism of rapidly quenched "austenitic" stainless steel samples can be safely attributed to so-called "delta-ferrite", a high-temperature bcc phase which occurs "above" the "gamma-loop" or fcc (austenitic) region of the stainless steel phase diagram. The amount of retained delta-ferrite, hence the strength of the sample's ferromagnetism, can be used as a measure of the rapidity of the quench. Much to our surprise, the drop-tube processed samples were generally more strongly ferromagnetic than even the hammer-and-anvil-quenched ones. Either the samples experienced very rapid melt quenching (faster than about 10^6 K 5^{-1}) or the results of deeply undercooled solidification must be regarded in a different light from those of rapid melt quenching.

During the Sixth Quarterly Period magnetic results acquired previously were put into a form suitable for further analysis. As a result, the following data were able to be presented:

(1) Tables of Magnetic Susceptibility versus H and T for samples of the stainless steels AISI 310S, AISI 316, and Nitronic 40, and Nitronic 40W, (2) Tabulated Magnetization versus H at room temperature for AISI 316 Nitronic 40 and Nitronic 40W, (3) a set of optical metallographs for (i) annealed, (ii) splat quenched, (iii) drop-tube processed, AISI 316, Nitronic 40 and Nitronic 40W, (4) qualitative (i.e., unstandardized) X-ray diffraction results for Nitronic 40 indicating the presence of delta-ferrite.

3. PROGRESS DURING THE SEVENTH QUARTER

The Seventh Quarter has been particularly fruitful. Thanks to an infusion of additional funds it has been possible to conduct all the research planned, and more. Accomplished during the Seventh Quarter were the following tasks:

(1) Analyze the room-temperature magnetization (M)-versus-Field (H) data for the following samples/conditions:

AISI 316	annealed splat quenched drop-tube quenched
Nitronic 40	annealed splat quenched drop-tube quenched
Nitronic 40W	annealed splat quenched drop-tube quenched pendant-drop cooled.

(2) Conduct an X-ray diffraction analysis of a reference sample of splat-quenched Nitronic 40 to quantitatively estimate expected delta-ferrite which turned out not to be visible in the optical microscope

(3) Evaluate the results of an SEM/EDAX investigation already carried out on a sample of splat-quenched AISI 316

(4) Continue estimating an effective quench rate for stainless steel samples in the NASA drop tube

In addition, two papers entitled "Mictomagnetism in Austenitic Stainless Steels" and "Magnetic Studies of Rapidly Quenched Austenitic Stainless Steel Alloys" were presented at the International Cryogenic Materials Conference held in Kiev, USSR, during July 24-26. Abstracts of these papers have already been submitted to NASA. Some important results of the Seventh-Quarter research are presented below.

3.1 Room-Temperature Magnetization Data

Room-temperature magnetization (M) versus magnetic field (H) data for the alloys AISI 310S, AISI 316, Nitronic® 40 (henceforth "Nit40"), and Nitronic® 40W (henceforth "Nit40W"), are presented in Figures 1 through 4. The sample conditions depicted are:

(1) Annealed 1h/1050 C (AN)

(2) Hammer-and-anvil splat quenched (SQ)

(3) Electron-beam melted droplet cooled on the end of a wire, i.e., "pendant-drop cooled" (PD)

(4) Solidified after undercooling during free fall in the NASA drop tube (DT).

AISI 310S (Figure 1) is evidently very stable against ferromagnetic δ-ferrite precipitation. Such precipitation is not completely absent, although an expanded vertical scale is needed to demonstrate its presence in magnetic terms. No bcc regions large enough to provide bulk ferromagnetic properties are present. The AN-processed sample is, of course, simply paramagnetic but superparamagnetism is evident at room temperature in both the SQ- and DT-processed samples.

In all the other alloys M saturates in sufficiently high applied fields thereby providing evidence for various levels of ferromagnetic precipitation -- the bcc phase of Fe-Cr-Ni, presumably δ-ferrite in most cases. The abundance of bcc phase can be estimated from the saturation magnetization in the following way: According to Curtis and Sherwin*, the saturation magnetization of bcc Fe-Cr-Ni, composed of $f_{Fe,Cr,Ni}$ weight-fractions of Fe,Cr,Ni, is given by

$$M_s = 222f_{Fe} + 22f_{Cr} + 60f_{Ni}$$

in the units A m^{-1}/ρ_{SI}, when ρ_{SI} is the alloy's density is kg m^{-3} (this is also numerically equivalent to the moment expressed in cm^3 g^{-1} Oe). By comparing the measured saturation magnetization with the above-calculated value, the fraction of bcc phase can be immediately calculated. The results are given in Table 1.

3.2. X-Ray Diffraction Data

An alternative method of estimating the bcc-phase content of an fcc + bcc-phase mixture is to use calibrated X-ray diffractometry. The bcc-phase line intensities are compared with those from unalloyed bcc-Fe and the fcc-phase line intensities with those from AISI 310S, which is practically 100 percent fcc in all process conditions. An example of the application of this approach to the analysis of δ-ferrite abundance in splat-quenched Nit40 is given in Figure 5. In the experiments referred to, the reference sample of α-Fe was in the form of a coarse-ground wrought slab, while that of 310S had been splat quenched as had the Nit40 sample under investigation. The quantitative results of this measurement are presented in Table 2.

3.3. Results of the Magnetic and X-Ray Analyses

According to Table 1, the δ-ferrite content of SQ Nit40 by saturation-magnetization measurement is 28%; according to the X-ray analysis of Table 2, it is more than 50%. Magnetic measurements of PD Nit40W claimed 31% of δ-ferrite and the precipitate after electrolytic etching, was easily visible in the optical

* C. J. Curtis and F. C. Sherwin, Brit. J. Appl. Phys. 12, 334 (1961).

microscope. The δ ferrite detected magnetically in SQ and DT Nit40 and Nit40W was not observable optically after attempted electrolytic etching, either because it was the dominant phase present or because the quench rates concerned were too rapid to permit appreciable interdiffusion of solute to take place between the γ and δ phases.

There is an apparent discrepancy between the magnetic and X-ray results for SQ Nit40, cf. Tables 1 and 2. It must be remembered, of course, that while magnetization is a property of the entire volume of the specimen, X-rays sample only its surface layers. The SQ grains grow in a columnar manner from the chilled faces towards the center-planed the splat, obviously the outer layers chill most rapidly, and within them one would expect to find the highest density of ferrite. This result supports the original contention that the δ-ferrite content of a rapidly quenched "primary-δ" austenitic alloy can be used as an indicator of the quench rate experienced by SQ samples.

Finally we note that the δ-ferrite content of the DT-processed material is generally much greater than that of the SQ. Within the framework of a "melt-quenching" approach, this suggests that the equivalent quench rate accompanying DT solidification is much greater than that encountered in hammer-and-anvil SQ, i.e., faster than about 10^6 K 5^{-1}.

3.4. Sample-Compositional Stability

It has been argued that the observed results could be attributed to severe compositional changes accompanying possible sample overheating during levitation melting prior to sample-release at the top of the drop tube. Accordingly, the last experimental activity to take place this Quarter consisted of measuring principle-ingredient compositions, in the scanning electron microscope, of a representative group of samples. The results of the analysis, presented in Table 3, show that no significant compositional differences exist among identical alloys processed under different conditions. It can be concluded, therefore, that the results presented are valid indicators of the effects of the various processing conditions.

4. RECOMMENDATIONS FOR FURTHER RESEARCH

The results of the research conducted to date under the program have indicated that drop-tube processing represent an important technique for the preparation of massive samples in what appears to be very rapidly quenched conditions. Accordingly, a proposal for detailed examination of various classes of drop-tube-processed alloy was submitted on July 2, 1984. One of the stated goals of the contract extension under which this Quarter's research was conducted, was to prepare such a proposal.

Table 1. δ-Ferrite Abundances from Magnetization Measurement

	Composition*, wt.%, in terms of Fe, Cr, and Ni			Saturation Magnetization**				Estimated δ-Ferrite Content, wt.%		
				100% bcc,	Experiment					
	Fe	Cr	Ni	Theory	PD	SQ	DT	PD	SQ	DT
AISI 310 S	52.5	24.7	20.4	134	--	0.1_2	0.2_9	--	0.1	0.2
AISI 316	66.8	16.8	11.7	159	--	0.8	1.2	--	0.5	0.6_5
Nitronic® 40	62.4	20.2	7.3	147	--	28	128	--	19	86
Nitronic® 40W	62.6	20.8	6.5	148	31	53	139	21	36	94

* No information is available on how to include the Mn.

** The units are Am^{-1}/ρ_{SI}, where ρ_{SI} is the density in kg/m^3. The number of emu/g is numerically the same.

Table 2. δ-Ferrite Abundance in SQ Nitronic® 40 From X-ray Diffractometry

	Line Intensities (Arbitrary Units)			Estimated δ-Ferrite Content, vol.%
	SQ AISI 310S	α-Fe*	SQ Nitronic® 40	
Austenite (fcc) line	27.6 (30.7)**	absent	13.2	52 (57)**
Ferrite (bcc) line	absent	10.6	8.8	83***

* The α-Fe was in bulk form.

** Repeated diffraction scan.

*** Less weight should be attached to this value than to the above.

TABLE 3. COMPOSITIONS OF STAINLESS STEEL SAMPLES UNDER VARIOUS PROCESSING CONDITIONS

Alloy	Condition	Composition in Weight Percent, Fe	Cr	Ni	Si	S
AISI 316	AN	66.6	17.9	13.1	1.1	1.3
	SQ	66.6	17.8	13.2	1.0	1.3
	DT	66.7	17.4	13.2	1.3	1.5
Nit40	SQ	68.5	21.9	8.4	1.2	-
	DT	68.0	22.4	8.6	1.1	-
Nit40W	SQ	68.3	22.9	7.7	1.2	-
	DT	68.3	22.9	7.9	1.0	-

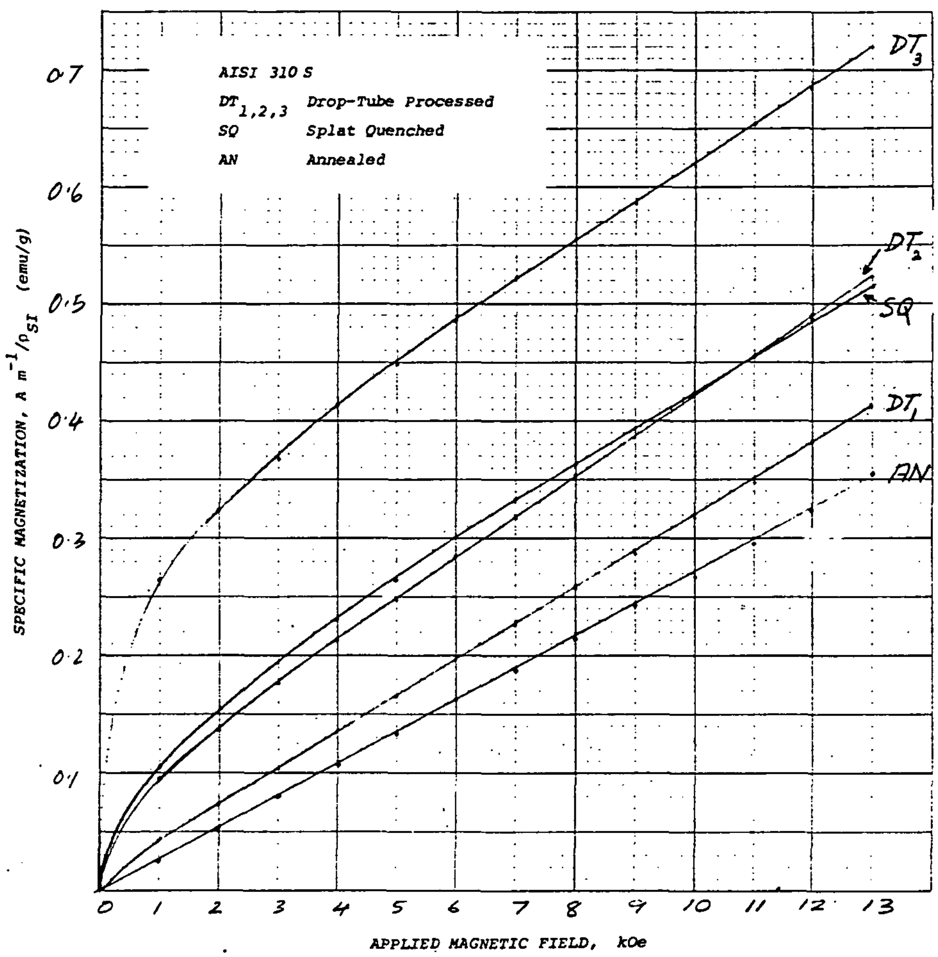

FIGURE 1. MAGNETIZATION VERSUS APPLIED FIELD STRENGTH AT ROOM TEMPERATURE FOR AISI 310S; THE SAMPLE MASSES ARE IN THE ORDER $DT_3 > DT_2 > DT_1$

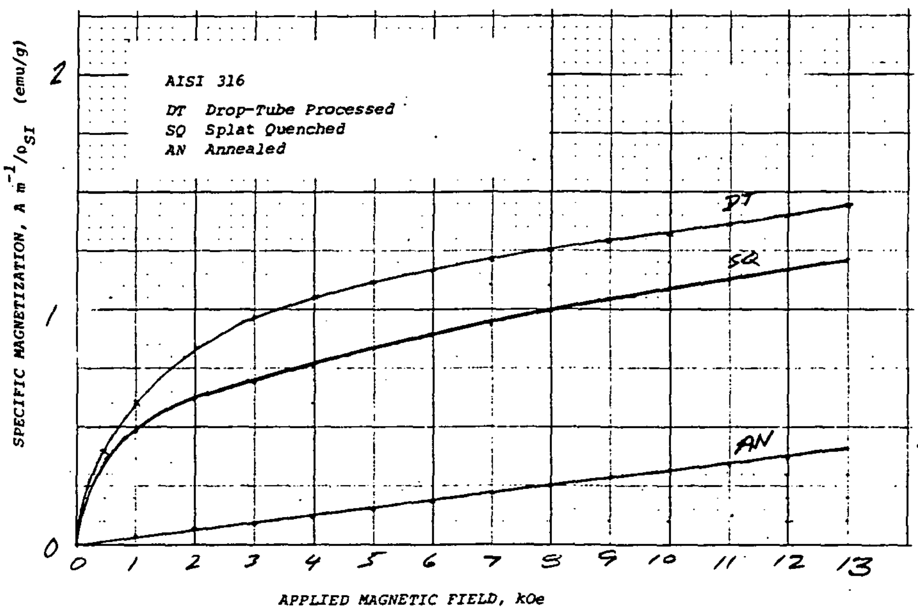

FIGURE 2. MAGNETIZATION VERSUS APPLIED FIELD STRENGTH AT ROOM TEMPERATURE FOR AISI 316

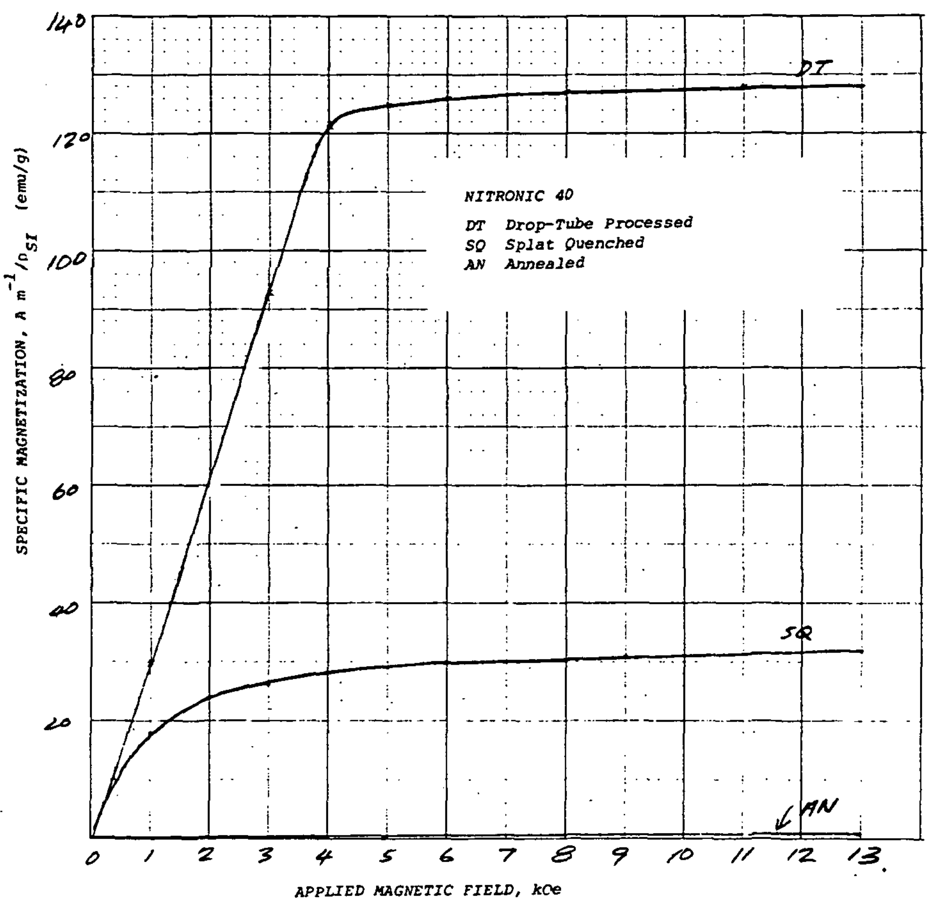

FIGURE 3. MAGNETIZATION VERSUS APPLIED FIELD STRENGTH AT ROOM TEMPERATURE FOR NITRONIC R 40

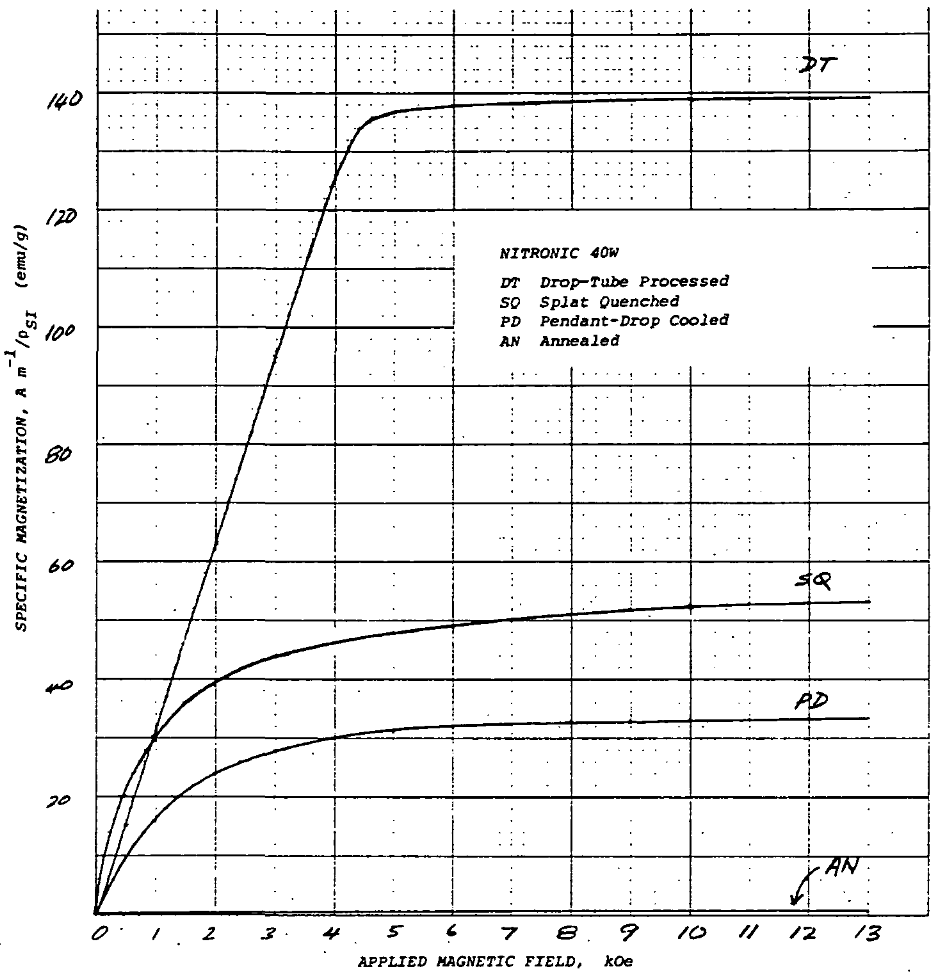

FIGURE 4. MAGNETIZATION VERSUS APPLIED FIELD STRENGTH AT ROOM TEMPERATURE FOR NITRONIC R 40W

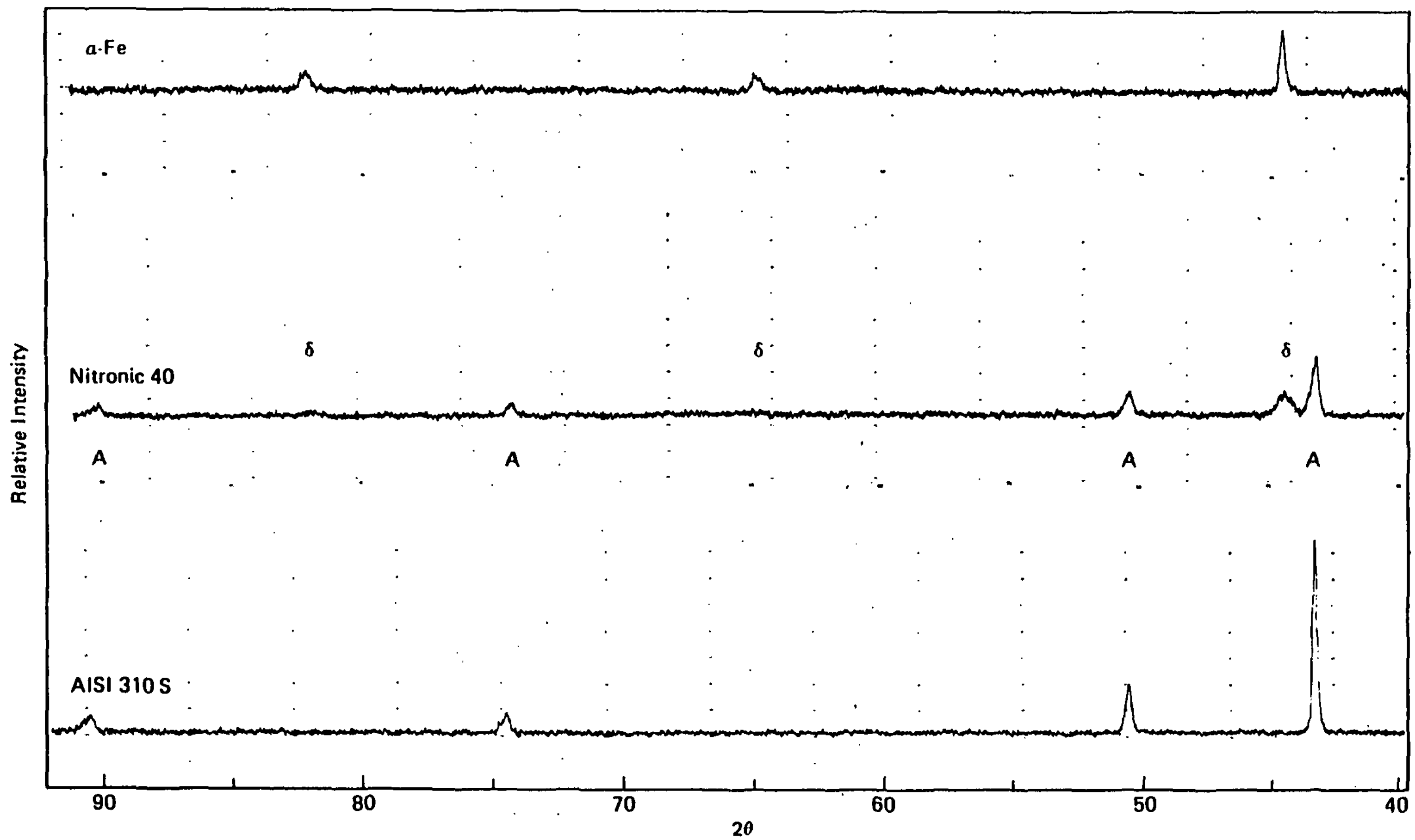

Fig. 5. X-ray diffraction analysis of the bcc-phase (δ-ferrite) abundance in a sample of splat-quenched Nitronic® 40 stainless steel. Using the same beam intensities, the principal line areas of α-Fe (100% "ferritic"), Nit40 (austenite+ferrite) and AISI 310S (100% austenite) are intercompared. X-radiation -- Cu K_α.